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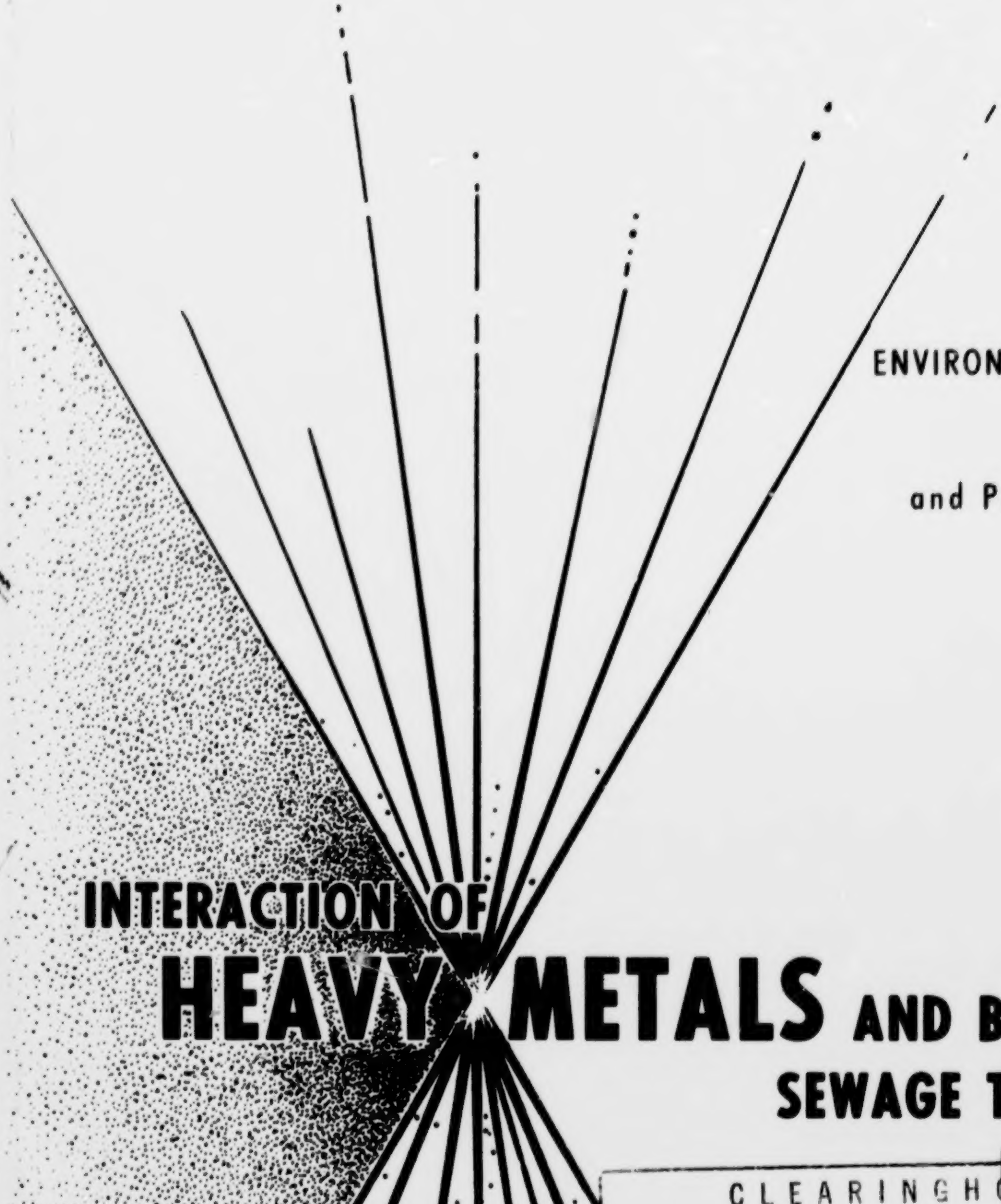

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INTERACTION OF HEAVY METALS AND BIOLOGICAL SEWAGE TREATMENT PROCESSES

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INTERACTION OF HEAVY METALS AND BIOLOGICAL SEWAGE TREATMENT PROCESSES 999-WP-22

INTERACTION OF HEAVY METALS AND BIOLOGICAL SEWAGE TREATMENT PROCESSES

Chemistry and Physics Section

Basic and Applied Sciences Branch

Robert A. Taft Sanitary Engineering Center

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Water Supply and Pollution Control
Cincinnati, Ohio

May 1965

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Public Health Service Publication No. 999-WP-22

FOREWORD

Research investigations concerning the interaction of metallic wastes on the biological sewage treatment processes were conducted at the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. Ten papers describing these results have been compiled into this report, which is to be used as a ready reference source.

While these assembled papers represent many man-years of time and effort, we do not consider the study to be exhaustive and believe that additional investigations are required. This volume is simply our best estimate of the response of the biological purification processes employed by municipalities to the metallic wastes commonly discharged to the treatment plants.

The work reported has been under the immediate supervision of three project leaders: Messrs. W. A. Moore, G. N. McDermott, and E. F. Barth. Through the investigations the need of careful pilot-plant operation and sustained analytical observation of plant performance have required the patient and sustained skills of many people. The assignments have been difficult, and we wish to recognize the proficiency and dedicated efforts of the following crew members: Messrs. J. N. English, B. V. Salotto, B. N. Jackson, W. E. Tolliver, H. E. Thomas, R. G. Santangelo, and J. L. Hinchberger.

In the field investigations, the project has been greatly aided by the vigorous interest of a group of progressive and cooperative plant operators. With gratitude and deep appreciation, we acknowledge the assistance of Mrs. D. Voshel, Grand Rapids, Michigan, Messrs. M. Phillips, Bryan, Ohio; W. E. Ross, Richmond, Indiana; and P. R. Carlson, Rockford, Illinois.

The entire project was coordinated by M. B. Ettinger, Chief, Chemistry and Physics Section, Basic and Applied Sciences Branch, Division of Water Supply and Pollution Control.

We are indebted to the editors of the *Journal of Water Pollution Control Federation* and *Proceedings of Purdue Industrial Waste Conference* in which many of the papers were published, and to the Natural Resources Institute, Ohio State University.

Paul W. Kabler, M.D.
Acting Deputy Chief
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Division of Water Supply and
Pollution Control

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ABSTRACT

This volume, a collection of 10 research papers originating at the Robert A. Taft Sanitary Engineering Center, describes the effects of chromium, copper, nickel, and zinc on sewage treatment processes. Results of pilot plant studies and full-scale municipal plants are given.

For each of the metals and combinations of metals studied, the effects on the aerobic and anaerobic treatment processes, under continuous dosage, are given. The data presented allow a reasonable estimate to be made of the amount of metallic wastes that a treatment plant can receive and accomplish the desired efficiency of treatment. The effects of slug discharges of the metals on the aerobic and anaerobic processes under pilot plant conditions and at municipal plants are presented.

The concentrations of the metals in the various sludges and effluents produced by a treatment plant are given. Metal balances conducted for each of the studies show the amount of metal removed by primary and secondary treatment.

INTERACTION OF HEAVY METALS AND BIOLOGICAL SEWAGE TREATMENT PROCESSES

INTRODUCTION

At the request of the National Technical Task Committee on Industrial Wastes, a series of investigations was undertaken because of the interest of major metal processors in the acceptability of industrial wastes in municipal sewage treatment. The initial overall objectives of the study were as stated at the beginning of Chapter I. The scope of the study has been enlarged to incorporate additional objectives, which include study of the effects of various metals on nitrogen transformations and the determination of the effects of the ratios of organic load to metal content on activated-sludge treatment.

The effects on the aerobic and anaerobic treatment processes, under continuous dosage, are given for chromium, copper, nickel, zinc, and combinations of these metals. Eight chapters deal with studies carried out on a pilot scale; two chapters are concerned with actual experience at operating municipal plants.

Each chapter has been taken from a completed research paper; thus, the reader may find repetition of some points common to the overall research. We hope that this repetition will reinforce those areas that we feel are important considerations in an investigation of this nature.

Mention of products and manufacturers is for identification only and does not imply endorsement by the Public Health Service and the U.S. Department of Health, Education, and Welfare.

CHAPTER I. CHROMIUM*

The objectives of these studies are:

1. To determine the extent to which sewage treatment processes can tolerate metallic wastes without losing efficiency in their treatment of the organic pollutants in sewage.

2. To determine the extent of removal of metallic wastes in sewage treatment plants and to follow their travel and concentration in various conventional sewage process units.

3. To develop modifications of sewage treatment procedures that will make them more tolerant of metallic wastes or more efficient in the removal of metals from sewage.

These objectives were established to serve a number of purposes. The data gathered will assist sewage disposal authorities in determining the quantity and characteristics of metallic wastes that may be accepted without fear of disrupting operation. Frequently, using municipal resources is the most efficient and desirable way for industry to dispose of its wastes. The community and its industries constitute a mutually dependent group; therefore ground rules are obviously desirable for determining optimum distribution of waste treatment effort between the municipal and industrial waste treatment facilities.

Numerous studies on the effect of metals on biological processes have been discussed in the literature in recent years. Unfortunately, practically all of these have been confined to bench experiments, which have not reasonably simulated plant situations, and the results obtained are not necessarily applicable to either the pilot plant or large-scale treatment of sewage. For this reason, the literature covering these experiments is not reviewed and only those references that apply to the present study are cited. Previous studies, for instance, do not show the effects of a given metal on the efficiency of a treatment plant when the metal is received in the influent sewage continuously or in slug doses.

In view of the incompleteness of data appearing in the literature, this study on the effects of various metals and combinations of metals on the activated-sludge process was undertaken on a pilot plant scale. Chromium, because of wide use in electroplating and tanning industries, was selected as the first metal to be studied.

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*Material in this chapter published previously in *Journal Water Pollution Control Federation,* Washington, D.C. 20016. See Reference 8.

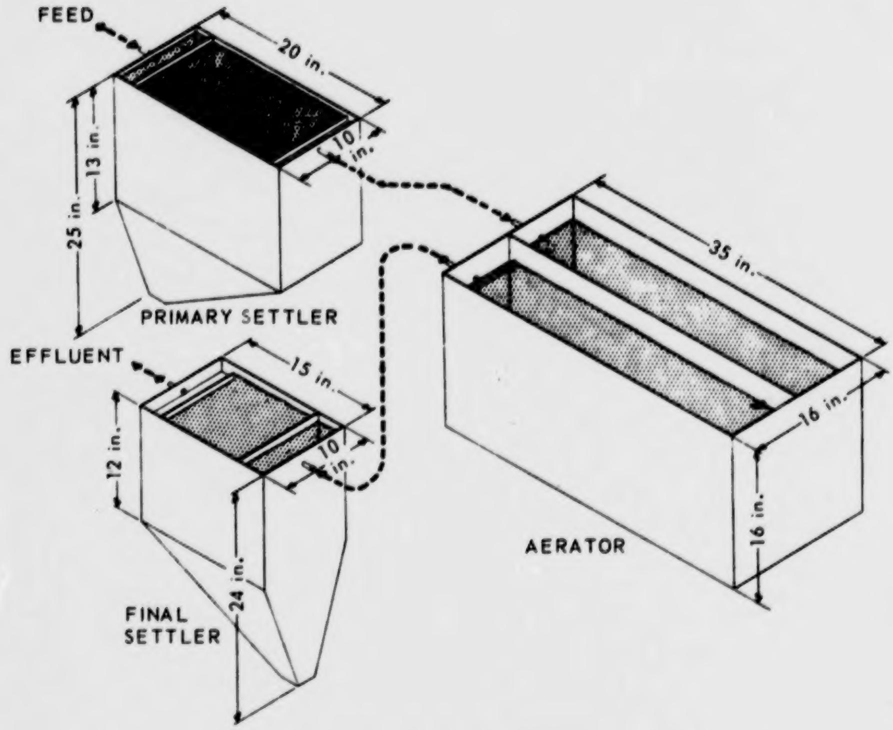


Figure 1. Activated-sludge pilot plant No. 1.

PLANT DESCRIPTION AND OPERATION

The shape and dimensions of the pilot model activated-sludge units used for studying the effect of continuous doses of chromium are shown in Figure 1. The units were constructed of thin sheet steel coated with a nonmetallic paint to minimize corrosion and the addition of extraneous metal ions to the sewage and to prevent plating of metal ion being added. The aeration tanks were narrow to limit short-circuiting and to attain spiral-type flow. The aerators were carborundum diffuser tubes, 2 inches in diameter.

Sewage was delivered to the plant from a small constant-head tank, which fed metering pumps of the rubber-tube nursing design. The constant-head tank was filled from the sewage storage tank on signal from a capacitor-activated liquid-level control. The contents of the storage tank were mixed continuously by means of a circulating system, which pumped from the bottom and returned to the mid-section of the tank. This sewage feeding system was developed to permit feed of a sewage of relatively constant strength with minimum loss of strength during feeding. The constant-head tank was kept mixed with a propeller-type stirrer. Primary sludge was drawn by gravity flow on a once-per-day schedule. Sludge from the secondary settler was pumped continuously by nursing-type pumps directly to the head of the aerator. Excess activated sludge was removed once daily as aerator liquor.

The feed rates, retention periods, loading factors, and other operating information are listed in Table 1. The quantity of air used was not measured because oxygen transfer by aeration in full-scale units is not reproducible in the size of model treatment plant employed. Sufficient air was supplied to maintain a dissolved oxygen level of 1 milligram per liter or more in the secondary settler supernatant. A concentration of suspended matter in the aerator liquor of 1,800 to 2,000 milligrams per liter was the general objective. Close control was not maintained in order to permit variation of the solids level in a random manner over the range of practical operation. The return sludge rate general objective was 30 percent of the raw sewage flow. This return was also permitted to vary in a random manner to cover the range of normal operation.

Table 1. DESIGN DATA AND LOADING FACTORS
ACTIVATED-SLUDGE PILOT PLANT

Item	Design used for continuous dose studies[a]	Design used for sludge dose studies[b]
Primary Settler		
Capacity,gal	13.8	4.6
Detention time, hr	2.3	1.2
Surface overflow rate, gpd/ft^2 surface area	125	142
Aeration Tank		
Capacity, gal	30.9	23.6
BOD loading, lb/day/1,000 ft^3 aeration tank volume	21–92	42–58
BOD loading, lb/day/lb VS	0.60	0.65
Aeration period[c], hr	5.0	6.0
Final Settler		
Capacity, gal	9.3	7.9
Detention time[c], hr	1.5	2
Surface overflow rate, gpd/ft^2 surface area	192	102

[a] Feed rate, 147 gpd.

[b] Feed rate, 95 gpd.

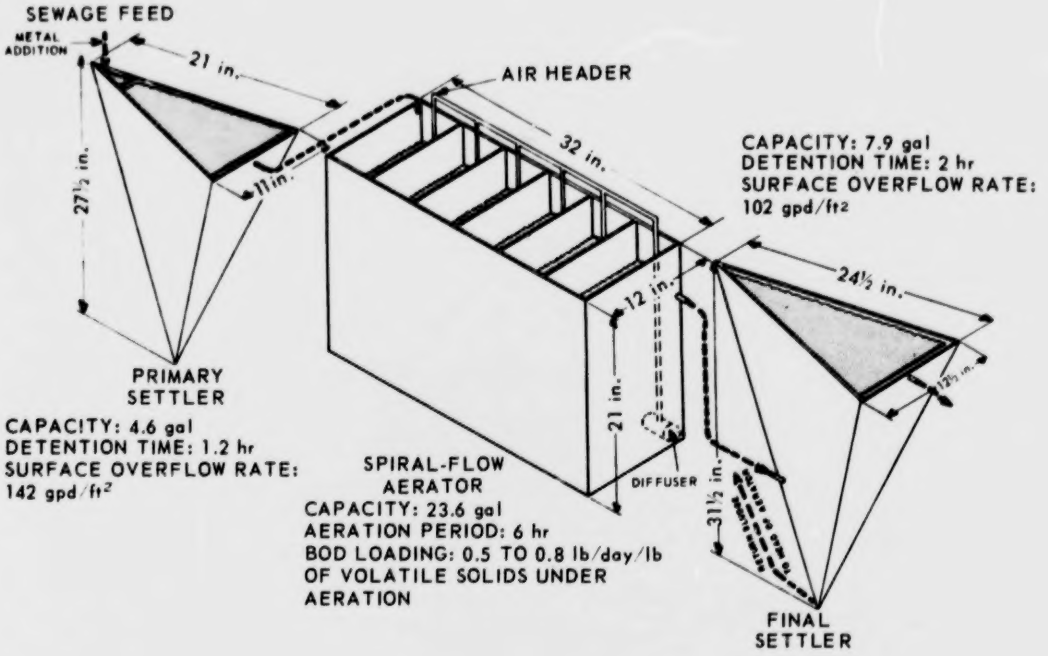
[c] Based on total tank volume and waste flow; return sludge not considered.

The metal was fed as a solution of potassium chromate by means of a capillary tube control on a constant-head vessel. A constant level of chromate solution in the feeder was attained with a Meriot bottle system, in which the flow of air into the bottle to replace discharged fluid is governed by the water level in the constant-head vessel. The feeder delivered 0.6 milliliter per minute of chromate solution to the tube carrying sewage to the primary settler just at its entrance to the settler.

Variations in the chromium content of the feed were generally less than 10 percent.

New Design

The activated-sludge units shown in Figure 1 accomplished satisfactory treatment; however, certain operating problems were present. The hoppers of the primary and secondary settling tanks retained small portions of sludge, which had to be moved to the drain by manual scraping. The accumulated sludge in the secondary settler was removed by hand twice a day and returned to the aerator. To maintain even airflow distribution along the aeration chamber was not practical, and this uneven airflow caused a longitudinal roll in the aerator much of the time and destroyed the desired spiral flow pattern. The paint blistered and exposed steel surfaces.



CAPACITY: 7.9 gal
DETENTION TIME: 2 hr
SURFACE OVERFLOW RATE: 102 gpd/ft²

CAPACITY: 4.6 gal
DETENTION TIME: 1.2 hr
SURFACE OVERFLOW RATE: 142 gpd/ft²

CAPACITY: 23.6 gal
AERATION PERIOD: 6 hr
BOD LOADING: 0.5 TO 0.8 lb/day/lb OF VOLATILE SOLIDS UNDER AERATION

Figure 2. Plastic activated-sludge pilot plant.

To solve these difficulties, a new plant of the design shown in Figure 2 was constructed. The units were constructed of acrylic plastic to avoid corrosion and plating factors. The shape of the settler was altered to create extremely steep sides to prevent prolonged holdup of any sludge. The concept of the design was to approximate a pie-shaped section of a circular sedimentation basin, the circumferential section being short enough to be approximated by a plane. The three walls were then sloped sharply inward to intersect at an apex at the bottom.

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The aerator was separated into six chambers by baffles to control longitudinal mixing and thereby more nearly approximate spiral flow design. There was one 1/2-inch-diameter circular opening in each chamber. The holes were placed alternately at the top and bottom and left and right side of the aerator so that the flow through each chamber was from the top at one side to the bottom on the other side, or vice versa. Carborundum air diffusers 2 inches in diameter were used.

The plastic unit was used for testing chromium slugs. Feed rates, retention periods, and other information are also listed in Table 1. The new settler design prevented prolonged sludge accumulation. A good flow pattern in the primary settler was achieved with a baffle near the inlet extending into the lower levels of the settler. The inflow tended to distribute itself in a horizontal layer near the lower end of the baffle and rise vertically to a thin surface layer, which moved horizontally to the weir. The achievement of such a flow pattern in the secondary settler was elusive. Regardless of how the settler was baffled, the inflow of aerator liquor caused a pronounced roll in the settler when the feed was near the surface. Operation with minimum roll was achieved by placing the inlet at about one-third the depth above the apex. In normal operation, the incoming sludge could be observed to settle as a layer at the interface of the sludge and the supernatant, and to fall as a slug vertically down to the return line. A thin film of sludge that accumulated at times on the sloping walls was squeezed free each day. All studies of the aeration phase of treatment, in these studies, were at room temperature, approximately 20° C.

The digesters were 5-gallon glass carboys equipped with gas collectors of the water displacement type. The digesters and gas collectors were housed in a constant-temperature room maintained at 30°C. The digesters were fed once a day with scheduled quantities of primary and excess activated sludge in the ratio of 64 percent primary sludge and 36 percent excess activated sludge on a volatile solids (VS) basis. The ratio of volatile solids in the primary and excess activated sludges was estimated, when the study was started, as likely to approximate actual production of the pilot plant. This proportion proved to agree within about 3 percent to the proportions actually produced in the unit receiving chromium.

Operation

The digesters were thoroughly agitated once a day by hand, and a volume of mixed digester contents equal to 1/26 of the digester volume was withdrawn. Thus, the average detention time in the digester was kept constant at 26 days. The digested sludge withdrawn was, therefore, what would be the combined supernatant and digested sludge of normal operation; the solids content was correspondingly low, ranging from about 0.5 to 1 percent. This concentration of solids was necessary to facilitate sampling.

The withdrawal of sludge and supernatant from the digesters used for testing the effect of slug doses of chromium was handled in a different manner. A volume of supernatant exceeding the scheduled sludge feed was withdrawn before mixing. The sludge was then fed and the liquid volume made up to a constant level with supernatant just previously withdrawn. Digested sludge was not removed from these units during the short test period.

The digesters were fed in the early weeks of operation at a rate of 5 grams per day of volatile solids; later this was increased to 10 grams per day. It was necessary to estimate the quantity of seed sludge corresponding to a balance of these feed rates and retention periods at the start of each study. Several months' operation was required before the sludge quantity in the digester actually levelled off. Digester loadings and operating data are listed in Table 2.

Table 2. DESIGN DATA AND LOADING FACTORS FOR DIGESTERS

Capacity, ft^3	0.67
Detention, days	26
Volatile solids loading, $lb/day/1,000\ ft^3$ digester volume	33

Sewage Feed

Concurrently with the design and construction of the pilot plants, an economical and adequate means was sought to fortify the sewage received in the experimental wing. This sewage, while of domestic origin, had an average biochemical oxygen demand (BOD) of about 75 milligrams per liter because of high ground-water infiltration. Various mixtures of supplemental foods were evaluated for use in changing the BOD and behavior patterns of the sewage to conform to ordinary domestic sewage characteristics. The cheapest suitable food was ground dog food. Various brands of dog food were tried before one was finally selected. Four hundred grams of the meal was allowed to soak overnight and then homogenized in a large blender. This homogenate was added to a 325-gallon tank of raw sewage. The addition of this supplement raised the average BOD to about 260 milligrams per liter, and the sewage so produced showed characteristic behavior.

Analytical Methods

With the exception of the determination of solids in primary sludge, aeration liquor, digested sludge, and the determination of chromium, the methods used in the study conformed to those given in *Standard Methods* (1).

In the case of sludge solids, the aluminum disc was not used and the sludge was filtered directly on a Buchner funnel with No. 40 Whatman paper.

The determination of total chromium in the raw sewage and various units of the plant (including digesters) was carried out by two variations of the basic procedure with essentially the same results. In both cases the organic matter was destroyed by fuming with H_2SO_4 and HNO_3. In this determination it has been postulated that a loss of chromium occurs (if Cr^{+6} is present) in the presence of chlorides and, therefore, all chromium should be reduced to the trivalent state prior to destruction of the organic matter. Just what concentration of chlorides must be present for this loss to occur, however, has never been thoroughly investigated. From some unpublished results the lower limit has been set at about 100 milligrams per liter, this concentration being higher than that normally encountered in this study. In the presence of organic matter, Cr^{+6} is rapidly reduced to the trivalent state on boiling with an H_2SO_4-HNO_3 mixture. With sludges, particularly digester sludge, the sample had to be fumed several times with this acid mixture before all organic matter was destroyed and a clear residue obtained. In one modification used, the Cr^{+6} was first reduced with sulfite and the sample was taken to fumes the necessary number of times to destroy the organic matter and then fumed for 15 minutes without being taken to dryness. The digestate was then diluted and the trivalent chromium oxidized with $KMnO_4$ (the excess of which was then destroyed with sodium azide). The solution was filtered through a sintered glass crucible, and the chromium determined on the whole or aliquot (depending on its concentration) using diphenylcarbazide. Absorbance readings were made on a spectrophotometer after 5 minutes, but not later than 15 minutes. The other modification used, consisted of destruction of the organic matter in the usual way and then fuming to dryness. The residue was taken up in 1-1 H_2SO_4, boiled, and then diluted. The silica was filtered off, and the filtrate made up to volume. The chromium in an aliquot was then oxidized with $KMnO_4$, and the color developed in the usual manner. As stated previously, both modifications gave essentially the same chromium recovery.

High concentrations of chromium were determined by oxidation of the trivalent form to Cr^{+6} after destruction of the organic matter. The hexavalent chromium was then titrated with a standard solution of ferrous ammonium sulfate using "ferroin" as the indicator.

In plant operation and special studies, in addition to the determination of total chromium, it was necessary to determine hexavalent chromium. This was especially true at the higher chromium feed rates. In determining hexavalent chromium, the sample was filtered by means of a membrane filter. This filtrate was perfectly clear, and hexavalent chromium could be determined with no difficulty in the usual manner.

SAMPLE COLLECTION AND PRESERVATION

Samples for efficiency studies of the unit continuously receiving chromium and the control unit were collected by hand at approximately hourly intervals and composited for a 7-hour period. The samples were refrigerated during the compositing period and held in a refrigerator overnight before analysis on the following day.

Samples for studies of the effect of slug doses of chromium were collected by means of a swing-tube solenoid-actuated automatic sampler. The samplers diverted the stream to be sampled to a compositing carboy on signal from a timing device. The timing device was set to collect the flow during about 2 seconds of each minute. The compositing periods are reported with the experimental data. These samples were kept in ice chests or refrigerated prior to analyses.

For purposes of material balances for chromium in the continuously dosed unit, samples of the effluent were collected continuously, 24 hours per day, 7 days per week, by means of an automatic sampler. The effluent samples were composited over 7-day periods. The 7-day accumulation of sludge was placed in a large tank and stirred mechanically prior to and during withdrawal of a sample. Samples of the mixed liquor at the beginning and end of the compositing periods were collected by dipping equal small quantities at regular intervals along the length of the aerator.

The digesters were routinely sampled for their mixed contents. The digesters were shaken vigorously by hand preceding and during a withdrawal of the samples.

EXPERIMENTAL DATA

Continuous Feeding

Two basic problems were present in this study: (1) the concentration at which the effects of a given metal ion are felt when received continuously in the influent of an activated-sludge treatment plant and (2) the concentration necessary to have an immediate effect on a plant and the time required for this plant to recover from a slug dose of the metal in question.

The effects of five concentrations (from 0.5 to 50 mg/l) of hexavalent chromium were studied. The two lowest concentrations were fed for approximately 1 month while the other three were studied for at least a 6-week period. The effects on BOD, chemical oxygen demand (COD), and suspended solids (SS) removal are given in Table 3. This table shows that the average BOD loads in both the chromium-

Table 3. EFFECT OF HEXAVALENT CHROMIUM ON PLANT EFFICIENCY

Period covered	Cr^{+6} fed, mg/liter	No. of samples	Raw waste, mg/liter		Primary effluent, mg/liter		Reduction, %		Final effluent, mg/liter		Plant removal efficiency, %	
			Cr^{+6} fed unit	Control unit	Cr^{+6} fed unit	Control unit	Cr^{+6} fed unit	Control unit	Cr^{+6} fed unit	Control unit	Cr^{+6} fed unit	Control unit
Average BOD												
Aug. 29–Oct. 2	0.5	6	268	259	180	180	33.5	30.4	14.8	14.7	94.3	94.3
Oct. 3–Oct. 31	2.0	7	261	288	199	201	22.4	28.3	16.2	18.9	93.2	93.5
Oct. 31–Dec. 19	5.0	8	311	314	192	173	35.8	44.4	10.9	14.9	96.8	94.9
Dec. 19–Feb. 25	15.0	8	320	296	193	198	39.8	32.9	15.9	12.7	95.0	95.7
Feb. 25–Apr. 24	50.0	8	253	263	138	119	45.5	54.8	20.9	13.0	91.7	95.1
Average COD												
Aug. 29–Oct. 2	0.5	6	452	444	270	266	40.3	40.1	52.0	59.0	88.5	86.7
Oct. 3–Oct. 31	2.0	7	427	447	297	305	30.4	31.8	70.0	65.0	83.6	85.5
Oct. 31–Dec. 19	5.0	8	493	496	312	285	36.7	42.5	74.0	75.0	85.0	84.9
Dec. 19–Feb. 25	15.0	8	458	467	294	277	35.8	40.7	96.0	83.0	79.0	82.2
Feb. 25–Apr. 24	50.0	8	411	406	234	227	43.1	44.1	67.0	49.0	83.7	87.9
Average SS												
Aug. 29–Oct. 31	0.5	6	323	303	143	146	52.5	55.1	12.0	13.0	96.3	95.7
Oct. 3–Oct 31	2.0	7	242	254	138	130	43.0	48.8	20.0	9.0	91.7	96.5
Oct. 31–Dec. 19	5.0	8	312	316	157	144	49.7	54.4	12.0	13.0	96.2	95.9
Dec. 19–Feb. 25	15.0	8	267	267	135	119	49.3	55.4	13.0	9.0	95.1	96.6
Feb. 25–Apr. 24	50.0	8	277	270	115	114	58.5	57.8	12.0	10.0	95.7	96.3

fed and control units were essentially the same, the 5-day BOD comparing with what would be expected in a sewage treatment plant receiving primarily domestic sewage. The BOD removal in the primary tank is also normal with respect to larger-scale plant operation. No logical explanation can be offered for the higher BOD removal in the primary settler during the last period of operation since the data for both the control and chromium-fed units are uniformly higher. The overall plant removal of BOD also shows little difference between the two units during the first four periods. However, when 50 milligrams per liter of Cr^{+6} was being fed, the average BOD removal obtained was about 3 percent lower for the chromium-fed unit. Limited significance can be placed on this figure since during the feeding of 5 milligrams per liter of Cr^{+6} the unit showed an average BOD removal 2 percent higher than that from the control.

A COD check indicated that the presence of Cr^{+6} had little effect on the removal of organic matter except possibly during the last period when the removal by the chromium-fed unit averaged about 4 percent lower than that of the control. This could be due to the fact that during this period the final effluent was more turbid, the solids contained therein approaching colloidal size and, therefore, not being determinable as suspended solids.

We had thought that in the presence of organic matter the Cr^{+6} might be reduced to Cr^{+3}, which would serve as a coagulant at the prevailing pH of the sewage. This naturally would lead to higher solids removal in the primary unit; however, as shown in Table 3 there was no difference between the control and the chromate-fed units in solids removal in the primary tanks. Further, the actual solids removed are in line with those found in larger plants. This suggested that the Cr^{+3} was not being precipitated as the hydroxide and was not acting as a flocculating agent. Udy (2) points out that the hydrous oxide $Cr_2O_3 \cdot x\,H_2O$ is formed and may be either a positively or negatively charged particle, depending on the pH. Only 10 milligrams per liter of chromium was reduced and precipitated with the highest chromium feed. Some of the reduced chromium also passed out of the primary in the effluent. Table 3 indicates that the overall plant removal of suspended solids was high and that regardless of the chromium feed concentration, both units were equally efficient.

During the periods in which 0.5 and 2 milligrams per liter of Cr^{+6} were being fed, the concentration of soluble chromium in the final effluent was negligible. With the 5-milligram-per-liter feed, the hexavalent chromium was usually less than 1.5 milligrams per liter in the final effluent and the total chromium less than 2.5 milligrams per liter. When, however, 50 milligrams per liter was being fed continuously, the primary effluent usually contained about 40 milligrams per liter of hexavalent chromium and the final effluent, around 30 milligrams per liter. Only occasional spot checks were made of the hexavalent and total chromium. As will be discussed later, a way was found to reduce the chromium content of the final effluent to a much lower level.

In the effluent from the primary tank the chromium was present in both non-settleable precipitated and soluble forms. A further reduction of hexavalent chromium took place in the aeration tank. The activated-sludge particles served to adsorb and reduce a portion of the soluble chromium as well as the finely divided precipitated chromium. This caused a buildup of total chromium in the aerator. Table 4 shows that this buildup increased markedly with increasing chromium fed to the raw sewage when expressed on a milligram-per-gram-suspended-solids basis. There naturally was a fluctuation in this value because of fluctuation in the suspended solids content of the aerator. The values given in Table 4, therefore, are average values that express the chromium concentration at the various chromium feed levels. When the study was concluded, a concentration of 93 milligrams of chromium per gram of suspended solids, or 9.3 percent, had been reached.

Table 4. BUILDUP OF CHROMIUM IN PRIMARY AND AERATOR SLUDGES

Chromium level in feed, mg/liter	Avg total chromium in primary sludge, mg/g SS	Avg total chromium in aeration tank contents, mg/g SS
0.5	0.36	4.0
2.0	1.3	8.0
5.0	1.5	26.0
15.0	2.5	36.0
50.0	5.9	66.0[a]

[a] Highest concentration reached was 93.

Slug Dose Feeding

A number of instances of activated-sludge plants receiving chromium in slug doses are recorded in the literature. In one such case, reported by Jenkins and Hewitt (3), a maximum concentration of 320 milligrams per liter of chromium was received in the influent sewage. Edwards and Nussberger (4) report the occurrence of two slug doses of chromium at an activated-sludge plant. During the first slug dose the influent contained 430 milligrams per liter of chromium for approximately 30 minutes. The following day a second slug dose was received for approximately 2 minutes. During this latter period the influent sewage contained 1,440 milligrams per liter of chromium. The results of these doses were reflected in a higher BOD in the effluent and a cessation of nitrification.

In this study of the effects of slug doses of Cr^{+6} on the activated-sludge process, concentrations of chromium of 10, 100, and 500 milligrams per liter were used. These concentrations were fed over a period of 4 hours to activated sludge that had had no previous contact with chromium. During the first 12 hours, composite samples were taken over 4-hour periods and at intervals thereafter until the unit returned to normal operation. The plant efficiency before the slug dose was fed, had been followed for at least 2 weeks. The data as given in Table 5 show that the feeding of 10 milligrams per liter over a 4-hour period had no effect on plant performance. The rise in suspended solids in the effluent after 4 days was due to bulking in the secondary settler. When a slug dose of 100 milligrams per liter of Cr^{+6} was used, the plant efficiency, as measured by BOD removal, dropped about 3 percent during the first 24 hours. The drop in COD removal was greater. Recovery was rapid. This also was true for the suspended solids removal. When a slug dose of 500 milligrams per liter was fed over a 4-hour period, the effect was striking and

Table 5. PLANT PERFORMANCE IN SLUG DOSE STUDIES

Time of sampling or dosing	BOD					COD					Suspended Solids		
	Raw waste, mg/liter	Primary effluent, mg/liter	Percent removal (primary)	Plant effluent, mg/liter	Percent removal (total)	Raw waste, mg/liter	Primary effluent, mg/liter	Percent removal (primary)	Plant effluent, mg/liter	Percent removal (total)	Raw waste, mg/liter	Plant effluent, mg/liter	Percent removal (total)
Avg data prior to slug dose[a]	291	177	36.4	8.6	96.5	341	234	31.5	31.9	89.8	228	4.3	97.1
Feb. 12[b]	–	–	–	–	–	–	–	–	–	–	–	–	–
9 a.m.–1 p.m.	284	–	–	8.8	96.9	373	–	–	37.5	89.9	428	4.0	99.1
1 p.m.–5 p.m.	288	–	–	12.9	95.5	422	–	–	45.9	89.1	342	2.0	99.4
5 p.m.–9 p.m.	221	–	–	10.1	95.4	340	–	–	35.7	89.5	220	2.0	99.1
9 p.m.–9 a.m.	235	–	–	7.0	97.0	301	–	–	42.1	86.0	160	1.0	99.4
9 a.m.–1 p.m.	187	–	–	9.4	95.0	304	–	–	43.5	83.7	258	5.0	98.1
Feb. 16[c]	269	–	–	10.4	96.1	291	–	–	49.1	83.1	268	10.0	96.3
Feb. 18[c]	210	–	–	6.1	97.1	330	–	–	35.1	89.4	254	38.0	85.0
Avg data prior to slug dose[a]	200	–	–	7.1	96.3	292	–	–	44.3	84.8	154	2.0	98.6
Feb. 25[d]	–	–	–	–	–	–	–	–	–	–	–	–	–
8 a.m.–12 noon	179	–	–	6.0	96.6	260	–	–	37.6	85.5	116	14.0	87.9
12 noon–4 p.m.	223	–	–	11.5	94.8	279	–	–	56.0	79.9	158	3.0	98.1
4 p.m.–8 p.m.	213	–	–	14.8	93.1	299	–	–	74.0	75.3	115	3.0	97.4
8 p.m.–8 a.m.	201	–	–	14.7	92.7	272	–	–	62.0	77.2	188	10.0	94.6
Feb. 27[c]	230	–	–	8.2	96.4	372	–	–	51.0	86.3	144	4.0	97.2
Mar. 2[c]	324	–	–	10.8	96.6	375	–	–	58.0	84.5	258	2.0	99.2
Avg data prior to slug dose[a]	249	126	52.2	7.8	96.9	358	203	42.9	41.2	86.7	241	3.5	98.6
Mar. 31[e]	–	–	–	–	–	–	–	–	–	–	–	–	–
8 a.m.–12 noon	236	216	8.4	21.4	90.5	362	212	41.4	75.0	79.3	278	20.0	92.8
12 noon–4 p.m.	240	152	36.6	27.0	<89.0	352	206	41.5	64.0	81.8	256	19.0	92.6
4 p.m.–8 a.m.	205	137	33.1	28.0	<86.0	341	194	43.1	87.0	74.5	276	25.0	91.0
8 p.m.–8 a.m.	208	133	36.1	27.2	87.0	320	173	45.9	85.0	73.4	234	11.0	95.3
8 a.m.–4 p.m.	220	139	36.8	28.7	86.8	350	189	46.0	69.0	80.3	262	7.0	97.3
4 p.m.–8 a.m.	189	147	22.2	21.4	88.9	311	206	33.8	54.0	82.6	244	5.0	98.0
Apr. 3[c]	129	104	19.4	10.6	97.9	231	193	16.5	45.0	80.5	160	7.0	95.6
Apr. 6[c]	164	95	42.1	9.3	94.3	224	165	26.3	51.0	77.2	158	7.0	95.6

[a] Plant was operated for 2 weeks using new activated sludge.
[b] 10 mg/liter Cr^{+6} fed from 9 a.m. to 1 p.m.
[c] Denotes 24-hr composite sample.
[d] 100 mg/liter Cr^{+6} fed from 8 a.m. to 12 noon.
[e] 500 mg/liter fed from 8 a.m. to 12 noon.

was noticeable even during the period of feeding. Plant efficiency as measured by BOD and COD removal continued to drop for about 32 hours and then started to recover, and after 4 days the unit was again operating normally. The plant effluent was quite turbid for about 24 hours with a consequent increase in suspended solids.

One effect of hexavalent chromium on sewage systems noted by many workers is the inhibition of nitrifying bacteria. Jenkins and Hewitt (3) stress this point in their activated-sludge studies. Placak *et al.* (5) also suggest that this fact could be used in determination of the carbonaceous demand of sewage samples. It was found in this study that nitrification was inhibited for approximately 10 days even at the lower hexavalent chromium levels and then proceeded regardless of the concentration of chromium fed. Clearly, nitrifying bacteria can acclimatize to the constant presence of chromium.

Chromium Distribution and Recovery

From the weekly composites of primary sludge, excess activated sludge, plant effluent, and a composite grab sample of the aeration liquor at the end of the week and knowing the total chromium fed, the percent recovery of the chromium and its distribution were determined. The results for the various chromium levels used are presented in Table 6. For the two higher concentrations of chromium used, more than 50 percent of the chromium appeared in the plant effluent. This was both hexavalent and insoluble trivalent chromium. In the case of the 50-milligram-per-liter feed, more than 90 percent was in the hexavalent form. In accounting for the amount of chromium fed it must be recognized that sampling, laboratory analyses, and flow measurements are involved. Without careful attention to these factors, wide discrepancies in the percent chromium recovered can be obtained. The results in Table 6 show a fairly high degree of accuracy, considering the multiplicity of factors involved.

Table 6. CHROMIUM DISTRIBUTION AND RECOVERY [a]

Period	Hexavalent chromium fed, mg/liter	Total chromium fed, g	Total chromium primary sludge, g	Total chromium in excess activated sludge, g	Total chromium plant effluent, g	Net change of chromium in aerator solids, g	Chromium recovered, g	Percent accounted for
Aug. 18-Sept. 16	0.5	1.202	0.089	0.743	0.258	+ 0.064	1.103	92
Oct. 3-31	2.0	6.23	0.454	0.862	2.78	− 0.05	4.73	76
Oct. 31-Dec. 19	5.0	16.73	0.705	5.32	6.44	+ 3.17	13.1	78
Dec. 19-Feb. 24	15.0	56.1	1.45	15.4	31.5	+13.9	49.7	89
Mar. 9-30	50.0	183.0	2.44	16.8	162.0	− 6.9	178.0	97

[a] All values in table represent average of weekly balance periods.

Table 7. HEXAVALENT CHROMIUM REMOVAL WITH REDUCTOR

Sample date (May)	COD					BOD					Total chromium, mg/liter	
	Raw waste[a], mg/liter	Primary effluent, mg/liter	Reductor effluent, mg/liter	Final effluent, mg/liter	Total removal, %	Raw waste, mg/liter	Primary effluent, mg/liter	Reductor effluent, mg/liter	Final effluent, mg/liter	Total removal, %	Average plant effluent before use of reductor	Plant effluent using reductor
6[b]	484	344	268	99	79.5	427	248	154	27.3	93.7	–	7.0
13	467	303	253	95	79.7	362	185	152	26.7	92.5	39.7	3.3
15	548	307	172	74	89.6	383	212	105	26.0	93.2	–	4.7
20	536	384	204	55	89.7	567	309	278	18.9	96.6	–	1.7
29	467	327	243	56	88.0	452	235	258	18.4	95.9	–	2.0

[a] Average Cr^{+6} fed during run was 46.5 mg/liter.
[b] Reductor started May 1.

Chromium Removal With Biological Reductor

The large amounts of chromium passing the system with the 50-milligram-per-liter chromate feed were considered as a possible menace to receiving waters. A simple modification of the activated-sludge process to reduce chromium loss was sought. An auxiliary tank, to which both the primary effluent and return sludge were diverted, was installed. The effluent of this tank then went to the aeration basin. The tank was stirred, but not aerated so that it acted as an activated-sludge plant with chromate serving as the principal source of oxygen. The pilot plant was operated on this basis for approximately 1 month. During this period the average hexavalent chromium fed was about 47 milligrams per liter. Previous to the run, the average chromium in the plant effluent had been about 40 milligrams per liter. Table 7 shows that this method of operation resulted in the removal of more than 90 percent of the chromium fed. The chromium appearing in the plant effluent was all in the reduced insoluble state. The sludge in the reductor unit as well as that in the aeration basin became dark gray in color. Plant efficiency as measured by BOD removal, however, remained well above 90 percent during the period of operation. The BOD of the plant effluent decreased as the time of operation increased. In view of the progressive increase in plant efficiency, it is reasonable to believe that the plant could have continued operating satisfactorily indefinitely.

SLUDGE DIGESTION

Test Procedures And Results

In Table 8 the data obtained during the operation of the two digesters when the various chromium concentration levels were being fed are summarized. In both the primary and excess activated sludge the chromium was all in the reduced insoluble state. Coburn

Table 8. GAS PRODUCTION IN TERMS OF VOLATILE SOLIDS FED AND CHROMIUM RANGES IN DIGESTER

	Chromium level in feed of activated sludge plant, mg/liter	Chromium ranges in digester		CO_2 content of digester gas, %		Gas production, ml/g VS fed	
		mg/liter	mg/g SS	Chromium fed digester	Control digester	Digester fed sludge from chromium receiving unit	Digester fed sludge from control unit
Aug. 29–Oct. 2	0.5	11.2[a]–21.0	1.04– 1.69	26.0	25.0	769	622
Oct. 3 –31	2.0	21.0– 27.6	1.69– 3.16	27.0	26.0	710	680
Oct. 31–Dec. 19	5.0	27.6– 72.0	3.16–14.5	27.0	28.0	649	800
Dec. 19–Feb. 25	15.0	72.0–200.0	14.5 –28.0	26.0	26.0	666	704
Feb. 25–Apr. 24	50.0	200.0–420.0	28.0 –34.6	–	–	571	617

[a] Unit had operated at this chromium level for approximately 6 weeks before sufficiently reliable records were obtained.

(6) in his discussion on toxic wastes stated that the precipitated chromium transferred to the digesters along with the sludge would produce a toxic action thereby slowing up or stopping digestion. Table 8 shows that regardless of the chromium concentration in the digester, gas production was not affected, often being higher in the chromium-loaded digester than in the control. The percent CO_2 in both digester gases was found to be essentially the same. During the entire period of operation a digester was limed only once, the pH of both being fairly constant between 6.8 and 7.0. If trivalent chromium in solution had been added directly to the digester, deleterious effects could possibly have occurred. This was not done since substantial amounts of soluble trivalent chromium would require a pH of less than 4, which is not likely to be encountered in sludge pumped to a digester.

A digester was fed with freshly collected primary and excess activated sludge from the pilot plant while it was receiving 50 milligrams per liter of Cr^{+6} continuously. Both the total and hexavalent chromium content of these sludges are given in Table 9. This digester was fed on the 7th day and then from the 15th through the 21st days. The hexavalent chromium concentration (based on digester contents) was about 3 milligrams per liter. Figure 3 shows that this concentration of hexavalent chromium fed had no effect on gas production.

Table 9. CHROMIUM CONTENT OF FRESH SLUDGE FED TO DIGESTER[a]

Sludge identification	Hexavalent chromium content of feed			Total chromium content of feed		
	Concentration, mg/liter	Amount fed, mg	Suspended solids, mg/g	Concentration, mg/liter	Amount fed, mg	Suspended solids, mg/g
Primary sludge	38	11	1.0	330	99	8.7
Excess activated sludge	32	32	3.2	530	530	53

[a] Sludge taken from pilot plant while receiving 50 mg/liter hexavalent chromium continuously.

Another digester with no previous history of receiving chromium was fed fresh primary and excess activated sludge from the pilot plant that had received a slug dose of 100 milligrams per liter of hexavalent chromium. The chromium fed was both in the hexavalent

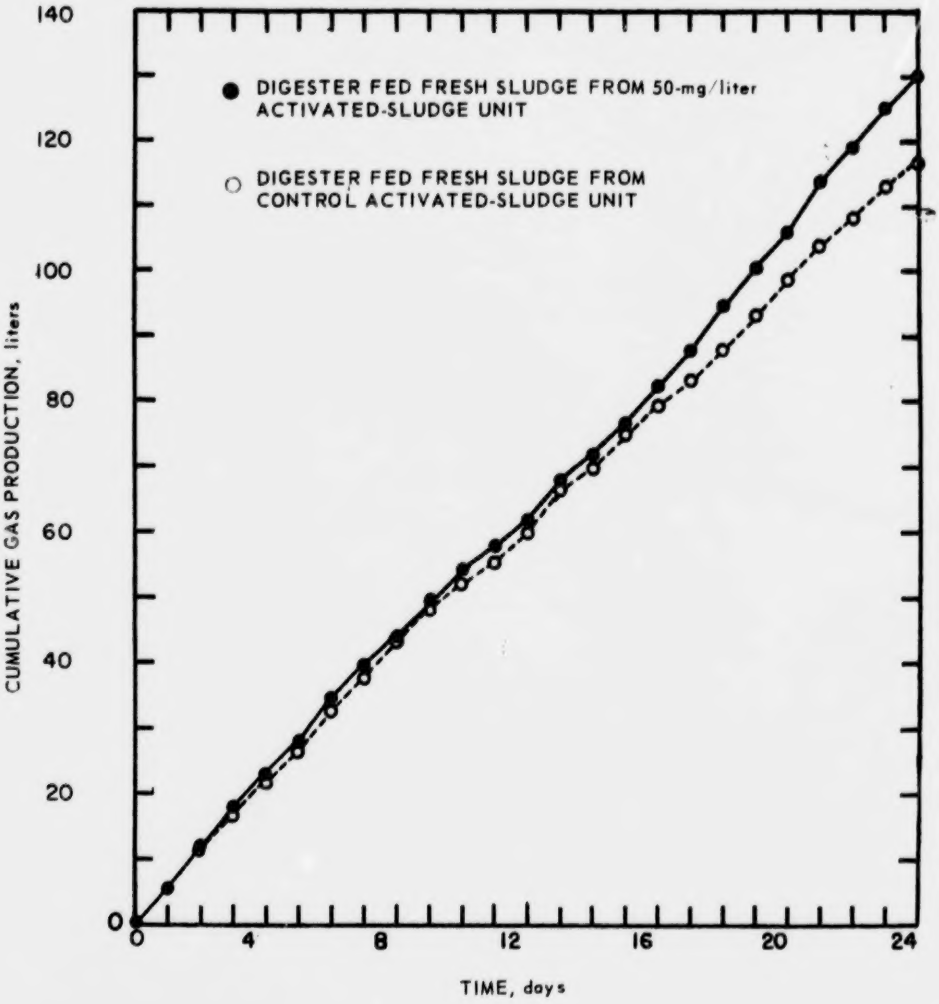

Figure 3. Effect on digesters of fresh sludges from activated-sludge plant receiving 50 mg/liter chromium continuously.

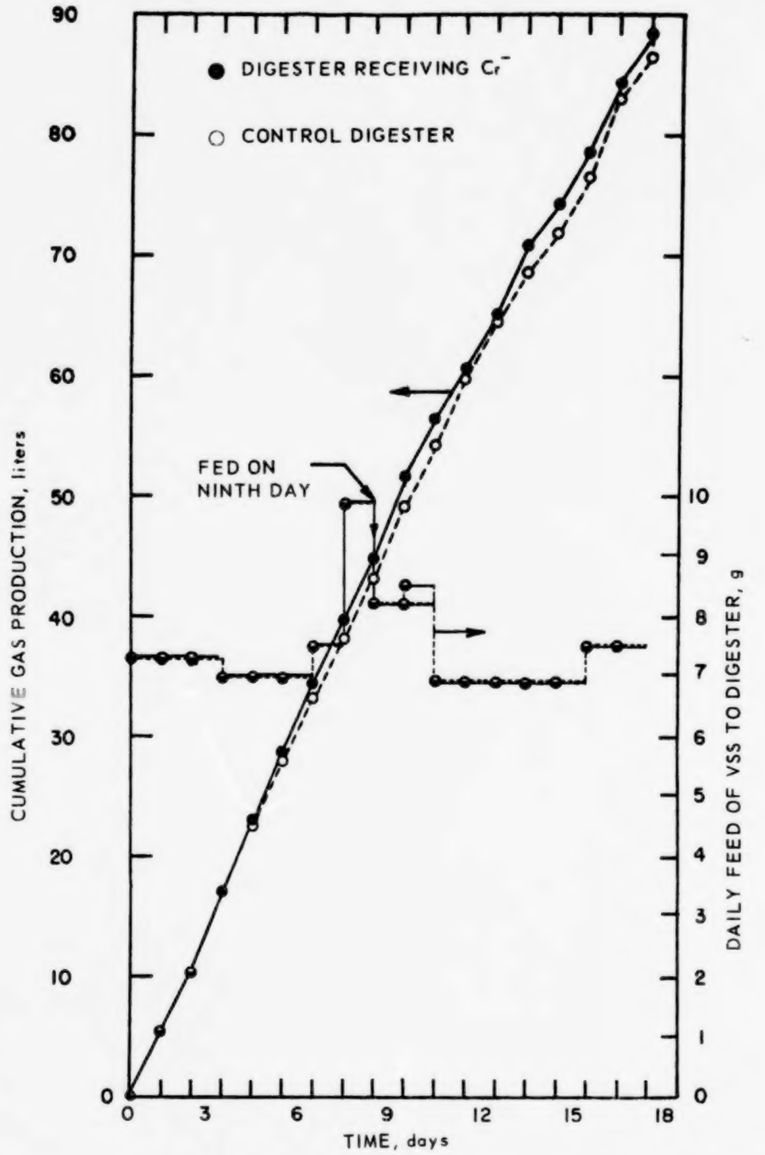

Figure 4. Effect on digester of sludge from 100-mg/liter slug dose to activated-sludge plant

and reduced form, and the feed contained 5.8 milligrams chromium per gram of suspended solids fed. Figure 4 shows that there was no noticeable difference between the operation of the two digesters. The average gas production for the chromium fed and control digesters per gram of volatile solids (VS) fed was 702 and 687 milliliters, respectively. Still another digester was fed with fresh solids from the pilot plant receiving a slug dose of 500 milligrams per liter of hexavalent chromium. No determinations of the hexavalent chromium were made, but in the case of this digester it would be about 30 milligrams per liter (based on digester contents). Here again, no effect was noted on gas production.

Since the feeding of reduced chromium or a combination of reduced and hexavalent chromium had no apparent effect on digester operation, the effect of a slug dose of hexavalent chromium alone was explored. This was done by adding directly 300 milligrams per liter (based on digester contents) of hexavalent chromium to a digester that had previously received chromium-containing sludge. Following the addition of this slug dose, the mixed liquor contained 700 milligrams per liter of total chromium. The supernatant, after thorough mixing, settling, and filtration, was analyzed and found to contain 60 milligrams per liter of hexavalent chromium. This high reduction in hexavalent chromium in such a short period seemed questionable; therefore, 300 milligrams per liter of Cr^{+6} was added to another digester sludge, and the same manipulative procedure was followed. Again a rapid loss of Cr^{+6} occurred; thus, the previous results were verified. A factor contributing to the rapid reduction of hexavalent chromium is the amount and condition of the solids present. This very rapid loss of Cr^{+6} can be accounted for largely by oxidation of the easily oxidizable compounds present and the bacterial utilization of oxygen available in the CrO_4^{-2} ion. The suspended solids content of the digester was 11,000 milligrams per liter. After 2 days the hexavalent chromium content of the digester had dropped to about 3 milligrams per liter. In Figure 5 the results of feeding this amount of hexavalent chromium in a slug dose are shown as well as the curve denoting the normal gas production obtained by feeding 9 grams of volatile solids (VS) per day. All gas production stopped for about 7 days and then gradually resumed, and the digester eventually returned to normal operation.

Since in the feeding of 300 milligrams per liter of hexavalent chromium the digester was able to recover in a comparatively short time, a slug dose of 500 milligrams per liter was tried. When this amount was added to another digester, all gas production stopped and the digester did not recover. Its contents were finally discarded at the end of 6 weeks. The likelihood of even 300 milligrams per liter of hexavalent chromium being pumped to a digester is very remote. A large percentage of the hexavalent chromium received at a sewage treatment plant would either be reduced in the primary or aeration basin, or pass out in the plant effluent.

There are two ways in which a digester could receive hexavalent chromium; namely, through the remote possibility of a slug dose or through receiving smaller amounts in the fresh solids. A further experiment was tried in which a digester was directly fed 50 milligrams per liter of hexavalent chromium (based on the digester con-

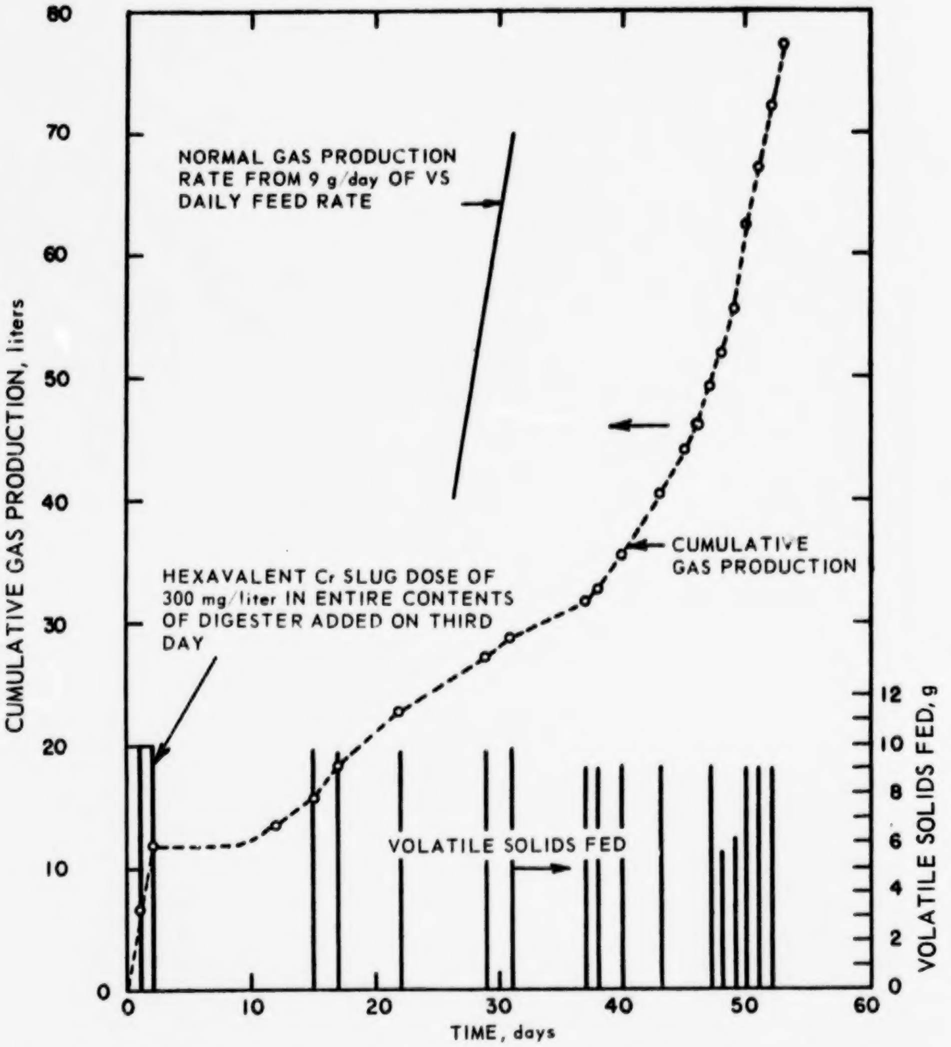

Figure 5. Effect on digester of 300-mg/liter slug dose of hexavalent chromium (Based on digester contents).

tents) daily for 42 days. The results obtained are shown in Figure 6. This amount of chromium was fed to one digester starting on the fifth day of observation. The two digesters were operating almost identically when the chromium feeding was started. Both digesters were receiving 10 ± 0.3 grams of volatile solids per day. After about 4 days of feeding 50 milligrams per liter of chromium, gas production started to decrease and at the end of 42 days the chromium-fed digester was producing about 75 milliliters of gas per gram of volatile solids fed, whereas the control was producing about 650 milliliters of gas. The total chromium concentration of the digester contents at the end of the experiment was 3,046 milligrams per liter. This effect was no doubt due to the cumulative effect of daily feeding of this amount of hexavalent chromium. This situation is, of course, not likely to arise in a sewage treatment plant.

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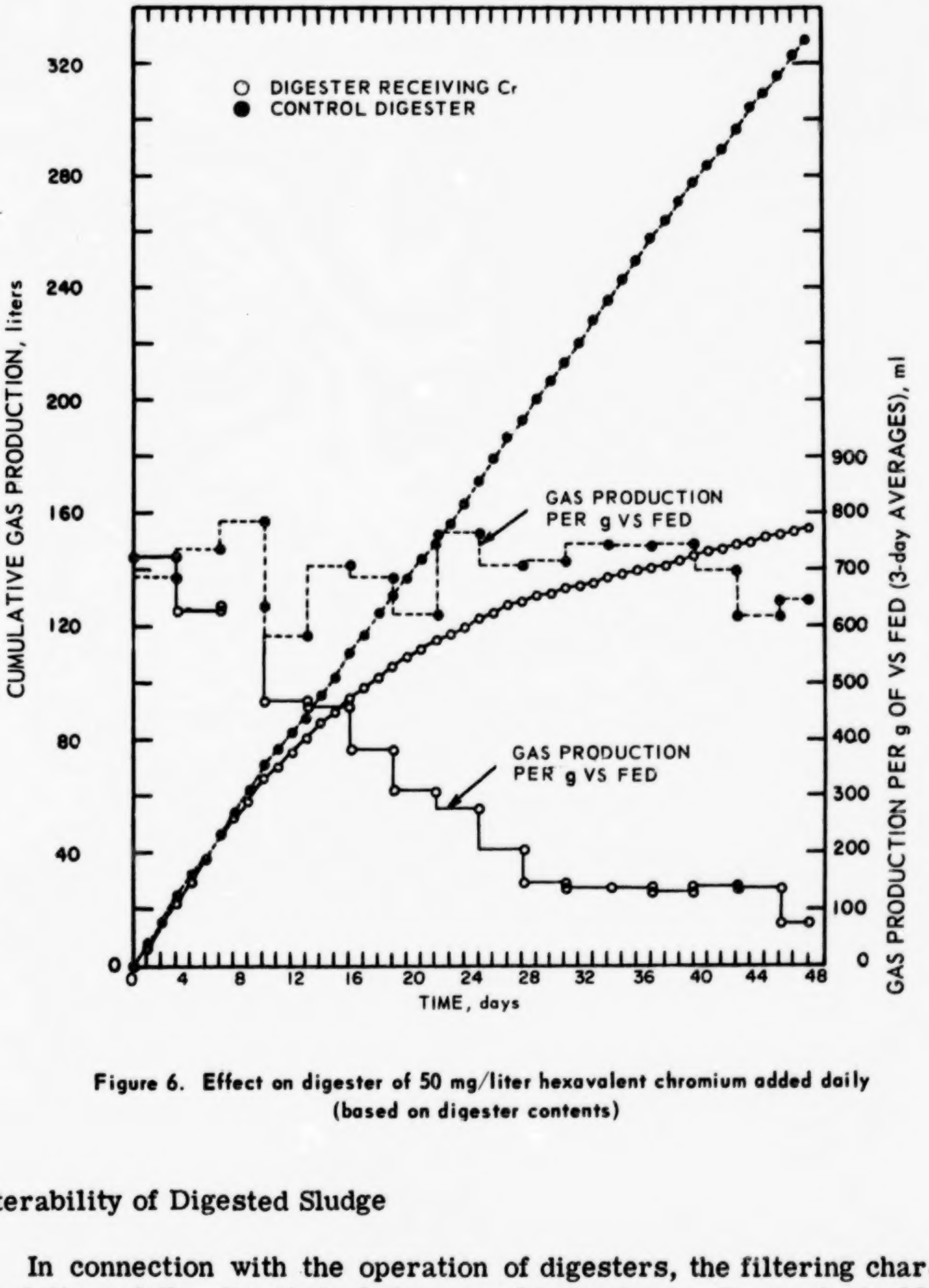

Figure 6. Effect on digester of 50 mg/liter hexavalent chromium added daily (based on digester contents)

Filterability of Digested Sludge

In connection with the operation of digesters, the filtering characteristics of the digested sludge are of importance. It was desirable to learn whether the presence of precipitated chromium would alter this property. The method of Genter (7) was followed in making the determination. In Figure 7, only a portion of the curves is shown. Three different sets of conditions were studied. In set 1 digested sludges from the chromium-containing and control digesters were filtered under vacuum (about 28 in.), and the volume of filtrate obtained was plotted against time. The "x" on the graphs denotes the time for cracking of the sludge cake and loss of vacuum. The chromium-containing sludge filtered much more rapidly than the control.

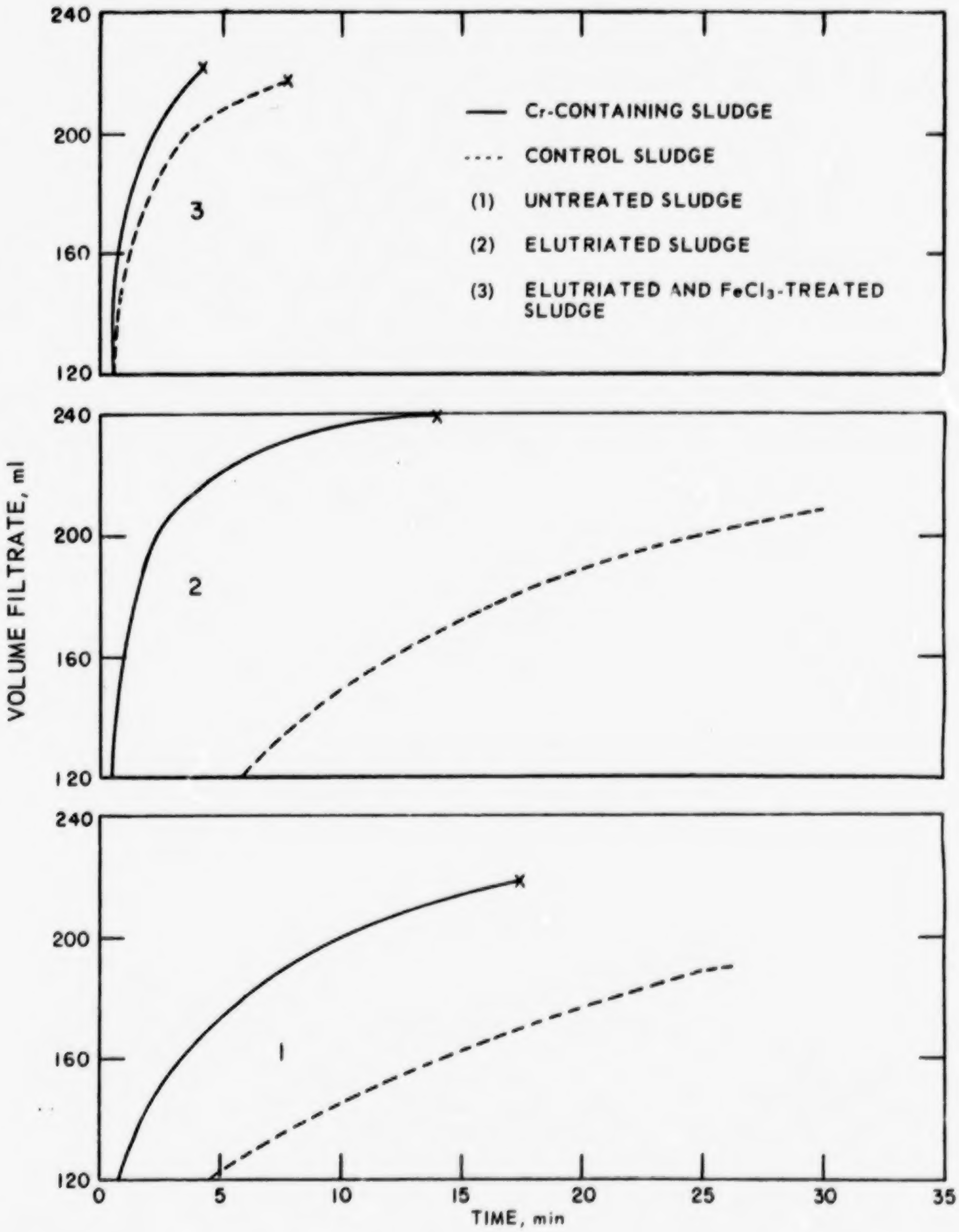

Figure 7. Filterability of digested sludges.

This, no doubt, is due entirely to the presence of precipitated chromium, which increases the permeability of the sludge cake and thus improves its draining characteristics. In set 2 both sludges were elutriated once with three times the sludge volume. Tap water was used to triple the volume. Elutriation shortened the time necessary for cracking in the chromium-containing sludge, but aided the control sludge only slightly. When both sludges were elutriated once and also treated with ferric chloride, as shown in set 3, the time for cracking was lessened greatly.

DISCUSSION OF RESULTS

Chromate may enter municipal sewage in many different ways. Perhaps most frequently it occurs in plating wastes, although it may have its source in tanning operations, in waters given corrosion inhibition treatment with chromate, or in aluminum-anodizing wastes. Since chromate retained in a sewage treatment plant is reduced to chromic chromium, it would also appear to be pertinent in relationship to the effect of this form of chromium on sewage treatment.

In addition to chromium, many plating wastes contain significant quantities of copper, nickel, zinc, cadmium, cyanide, and acid or alkali. Further, the wastes from a metal working industry are likely to be accompanied by large sewered losses of oil. These factors and many others that might enhance the toxicity of chromium have obviously not been considered.

Table 10. SUMMARY OF REACTIONS TO HEXAVALENT CHROMIUM

Chromium concentration, mg/liter	Feed methods, process	Effect on activated sludge	Short-time effects on digester	Sustained damage
50	Continuous feed to activated sludge plant.	BOD removal efficiency dropped about 3%	–	No damage noted
100	Slug dose to activated-sludge plant.	Plant recovered in about 20 hr, as measured by BOD removal efficiency	–	No damage noted
500	Slug dose to activated-sludge plant.	Plant recovered within 48 hr, as measured by BOD removal efficiency	–	No
50	Fed daily to digester; based on digester contents	–	Gas production dropped off rapidly. At end of 42 days only 75 ml/g of volatile solids was being produced.	Yes
300	Slug dose to digester	–	Gas production ceased to 7 days. Digester then gradually recovered.	No
500	Slug dose to digester	–	–	Yes, digester never recovered

A summary of results shown in Table 10 is indicative of the fact that, short of massive slug doses, chromate alone is unlikely to harm the operation of a sound sewage treatment plant.

Concentrations of hexavalent chromium of up to 0.5 milligram per liter were almost completely removed under conditions of the study. At a 2.0-milligram-per-liter feed, hexavalent chromium was occasionally found in small quantities in the effluent. With the 5.0-

milligram-per-liter and higher chromate feeds, variable-but-increasing fractions of the chromium passed through the system to emerge as either hexavalent or reduced chromium in the effluent. In view of the present mandatory limit of 0.05 milligram per liter of hexavalent chromium in drinking water, many situations exist in which total reduction of hexavalent chromium to insoluble trivalent chromium may be necessary. Where such chromium reduction and retention are required, a modification of the activated-sludge system using chromate as the oxygen source in an unaerated mixed liquor was found to yield total reduction of chromate accompanied by loss of small amounts of trivalent chromium dissolved or suspended in the final effluent.

While the systematic presence of chromate will halt nitrification for short periods, nitrification was evident even when the feed chromate level was 50 milligrams per liter. Chromate noticeably restrained the development of odor in the primary and the development of *Sphaerotilus* in the mixed liquor. The use of the chemical for this purpose is definitely not recommended.

The retention of chromium in the system occurred largely in the activated-sludge solids. The chromium content of the primary sludge solids (Table 4) invariably was lower than the chromium content of the mixed liquor solids, with the latter showing more than 10 times the chromium content of the primary sludge.

During the period when the biological chromate reduction and removal system was operated, the activated sludge contained up to 18.4 percent chromium on a dry solids basis. Obviously, reduced chromium has little or no toxicity to activated sludge. The digester operated well with as much as 3.5 percent chromium in the solids. Clearly, the total treatment system studied was resistant to and tolerant of all but the most drastic stresses by chromate.

CHAPTER II. COPPER*

In the study of the effects of copper on sewage treatment, the approach consisted of treating domestic sewage from a common source in three replicate activated-sludge pilot plants. Controlled additions of copper were made to two of the three plants; the third served as a control. The effects of copper were measured by differences in effluent quality. The pilot plants included primary settling, aeration with continuous sludge return, secondary settling, and anaerobic digestion. Thus opportunity existed for precipitation, reduction, and complexing, as might occur during primary settling in an actual situation before a biological process is reached. Effects are related to metal additions to the incoming sewage rather than to metals added to some specific plant component.

The activated-sludge pilot plants were designed to simulate standard activated-sludge plants of the spiral-flow type. The shape and dimensions of the activated sludge units, and a description of the sewage feed are given in Chapter I.

COPPER SOURCES AND FORM

Copper could be present in domestic sewage and industrial waste mixtures in several forms, depending upon its source and subsequent reactions. In the most common electroplating process, copper is deposited from cyanide baths. Copper in the form of copper sulfate is used for manufacture of copper articles by deposition from solution (electrodeposition), for recovery of copper from ore (electrorefining), and, to a lesser extent, for electroplating. Plating from copper pyrophosphate solution is also practiced. Plating baths are not simple solutions of the copper compounds, but commonly contain a group of materials among which are complexing agents. A listing of common forms of copper and auxiliary bath chemicals is given in Table 11, taken from Reference 9. In some of the baths the copper compound would be highly ionized to the simple cation, whereas in others the copper may be principally a soluble molecular complex or a complex anion. Copper is used as a catalyst in synthetic chemical manufacturing operations and may become associated with liquid wastes in some undetermined form. Copper chloride is used in mercaptan removal processes of the petroleum refining industry.

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*Material in this chapter published previously in *Journal Water Pollution Control Federation.* Washington, D.C. 20016. See Reference 13.

Table 11. INDUSTRIAL PLATING AND ELECTRO-DEPOSITING BATHS[a]

Operation	Typical bath constituents and proportions		Principal forms of copper in bath
	Compound	Concentration, mg/liter	
Plating	CuCN	26	
	NaCN	35	$NaCu(CN)_2$
	Na_2CO_3	30	$Na_2Cu(CN)_3$
	$KNaC_4H_4O_6 \cdot 4H_2O$	45	$Na_3Cu(CN)_4$
	Na OH to pH 12.6		
Plating	CuCN	75	
	NaCN	45.8	$NaCu(CN)_2$
	HCN	57.8	$Na_2Cu(CN)_3$
	NaCNS	9.8	$Na_3Cu(CN)_4$
	NaOH	15.0	
	KOH	21.0	
Plating[b]	CuCN	75	$NaCu(CN)_2$
	NaCN	84	$Na_2Cu(CN)_3$
	NaCNS	9.4	$Na_3Cu(CN)_4$
	NaOH	19	
Plating	Copper	22–38	
	Pyrophosphate	150–250	$K_6Cu(P_2O_7)_2$
	Oxalate	15–30	
	Nitrate	5–10	
	Ammonia	1–3	
	pH	8.2–8.8	
Electro-deposition and plating	$CuSO_4 \cdot 5H_2O$	150–250	$CuSO_4$
	H_2SO_4	45–110	
Electro-deposition	$Cu(BF_4)$	224–448	$Cu(BF_4)_2$
	HBF_4	15–30	
	H_3BO_3	15–30	
	pH 1.2-1.7		

[a] Taken from Reference 9.

[b] Plating solution used in this study for cyanide plating solution tests.

Investigation of the effects of each of these compounds and complexes of copper would be a formidable task; therefore, the study was limited to one copper compound that yields the simple copper cation in solution, e.g., copper sulphate, and to one copper complex, e.g., $Na_n\ Cu(CN)_n$, with the expectation that the data would satisfy the information need. Limitations on the permissible concentration of cyanides are common. Research on the effects of high concentration of cyanide complexes would not have practical meaning in such cases.

PLANT OPERATION

Sewage was fed to the units at a constant rate. Sludge from the final settler was pumped continuously to the head of the aerator at a rate of about 35 percent of the sewage feed flow. An automatic device, activated once per minute, diverted the return sludge 5 to 7 percent of each minute to a collecting vessel. This procedure wasted more than 25 percent of the suspended matter in the aeration tank each day. Capacity and loading factors for the units of the plant are given in Table 12.

Table 12. PILOT PLANT DESIGN DATA AND LOADING FACTORS

Unit	Loading factor	
Primary settler	Capacity Detention time Surface overflow rate	4.6 gal 1.2 hr 142 gpd/ft^2
Aeration tank	Capacity BOD loading Aeration period	23.6 gal 42–58 lb/day/1,000 ft^3 aeration tank volume 0.56 lb/day/lb VS under aeration 6 hr
Final settler	Capacity Detention time Surface overflow rate	7.9 gal 2 hr 102 gpd/ft^2

SAMPLE COLLECTION AND PRESERVATION

Samples for the routine measurement of BOD, COD, and SS removal efficiencies of the units fed copper and the control were collected by automatic mechanical samplers. The sampler diverted the stream to be sampled to a compositing carboy for 15 seconds at 15-minutes intervals. The samples were refrigerated and composited over 24-hour periods. Analysis was started within 3 hours after the end of the compositing period. Samples for studies of the effect of slug doses were collected by the same means. Compositing periods ranged from 4 to 12 hours to show peaks in effects.

Grab samples were taken for studies of the state of copper (in solution or suspension) for analysis of the nitrogen forms and for sulfide measurements. A complex sampling program was involved in making trial balances between copper fed to the unit and copper in the effluents plus accumulation of copper in the aerator. The balances were usually made for 1-week periods. Samples of each withdrawal of primary and excess activated sludge were composited over the balance period. Samples of the final effluent were collected by automatic sampler at 15-minute intervals and composited. Grab samples of the aerator liquor at the beginning and end of each balance period were taken for measurement of copper accumulating in the system.

ANALYTICAL METHODS

Unless otherwise stated, all procedures were essentially those outlined in *Standard Methods,* 11th Edition (10). Specific details were as follows:

Biochemcial Oxygen Demand

The initial and final dissolved oxygen measurements were made by the Alsterberg azide modification of the Winkler Method. Desired concentrations of the samples were prepared by the cylinder dilution technique. All BOD data reported are for samples incubated 5 days at 20° C.

Chemical Oxygen Demand

Primary feed and primary effluent samples were assayed by use of 0.25 N dichromate. Final effluents were assayed by use of 0.025 N dichromate. Silver sulfate catalyst was not used. No correction for chloride was made. Chlorides in this sewage were normally about 40 milligrams per liter.

Copper

Two methods of determining copper were utilized. High concentrations were determined by the usual iodimetric titration. Low concentrations were determined by the colorimetric cuprethol method. The organic matter was destroyed by fuming with sulfuric and nitric acid. For determining soluble copper, the sample was passed through an HA45 Millipore membrane. Copper in some forms will pass through the Millipore filter, but will not react with the cuprethol. Digestion to destroy complexes is necessary to determine total soluble copper in such samples. When copper in the filtrate reacts with cuprethol without digestion, it is termed reactive soluble copper.

Cyanide

Distillation as described in Reference 10 was used for preliminary screening to separate the cyanide from interfering substances. Each sample was refluxed for two 1-hour periods. The sum of the cyanide determined in each of the two 1-hour periods was reported as the total cyanide. Complexed copper cyanide is slow to be released and swept from the sample. At low cyanide concentrations the efficiency of recovery of the cyanide from copper complex in 2 hours of reflux would be especially low. Cyanide in the distillate at levels above 2 milligrams per liter was determined by $AgNO_3$ titration. Lower cyanide levels were determined by the pyridine-pyrazolone colorimetric method.

EXPERIMENTAL DATA

Metals are present in sewage and industrial waste mixtures because of sporadic receipt of metal-bearing wastes at the treatment plant, such as those that would result from occasional dumping of a spent plating bath or continuous losses of metal solutions from routine operations (slug discharges being avoided). A combination of the two is most probable. In consideration of these situations, investigations were made of effects from feeding copper at constant concentrations for periods up to 4 months and effects of doses of a few hours duration. In the continuous feeding studies, periods of 2 weeks or more were allowed between the initiation of a continuous metal feed and the collection of the first samples. This permitted time for possible acclimation or natural selection to occur. For the short-duration slug-dose tests, 4 hours was selected as the metal feeding period on the basis that it would approximate the drain time of a vat of plating solution. The routine slug-dose runs were made on biological sludges that had not previously received metal-bearing wastes.

During the continuous-feeding runs at each copper level, from 12 to 35 twenty-four-hour composite samples of the feeds, primary effluents, and final effluents were collected and analyzed. Differences in sewage feed characteristics among the plants were usually not greater than variations attributable to sampling and analytical accuracies. Characteristics of the sewage feed for each series of experiments are given in subsequent sections. The sewage feed was generally near or slightly below pH 7, and the final effluent was about pH 7.5. Removals accomplished in primary settling tanks were typical of sewage treatment plants.

The results are presented subsequently in four sections differentiated by the copper compound fed and whether a slug dose or a continuous metal feed was used. Data on the effluents are presented as cumulative percentage frequency curves. These curves permit presentation of the complete data and make comparisons of variations convenient. Comparison of effluent characteristics of a metal fed unit and the control on a day-by-day basis, that is, on samples collected simultaneously, showed little coordination in variations. For example, when the COD of the control plant effluent was high, that of the metal fed unit was not consistently in the higher levels of its variation range. This observation is in accord with reported experience (11) in operation of 12 replicate trickling filters in which there was no significant correlation between day-to-day variations in sewage feed and that of the 12 effluents, nor was there significant correlation among the 12 effluents on a day-to-day basis.

Most of the frequency distribution curves shown are arithmetic plots. Trials indicated that for much of the data, the use of standard probability paper, either arithmetic or logarithmic, was not helpful.

In some instances it was necessary to define statistically the expectancy that differences in the data would result by chance. In these cases probability paper was employed as part of the statistical analysis to test the normalcy of distribution of observations.

Consideration was given to the possibility of the cyanide radical *per se* exerting a damaging effect. Previous investigations have shown that activated sludge that has become acclimated and adapted to a feed containing cyanide would perform at normal efficiency and would remove the cyanide (12). To be certain that this observation was applicable to the exact circumstances of the metal studies, a short study was made with the addition of sodium cyanide alone to the sewage.

The rate and extent of biological acclimation to the presence of copper have important bearings on the experiments and actual occurrences. In the case of cyanides, not only is acclimation involved, but the rate of development of bacteria capable of utilizing the cyanide influences the extent and duration of damaging effects. Theoretically, the utilization of the cyanide radical could be accompanied by increasing damaging effects as the metal is released from the complex. It seems probable that the slug discharges would occur where metal-bearing wastes were normally present to some extent. Whether a system acclimated or adapted to a low level would be acclimated or adapted to a slug level five times greater or 10 times greater than the normal low level is also of interest. Although such questions were not investigated exhaustively, some data pertinent to the phenomena were obtained. Biological sludges acclimated to low metal concentrations were used in a few slug dose runs. Also in three of the continuous metal-feeding tests, sampling was initiated simultaneously with the start of a continuous metal-feeding run; thereby, information was gathered on treatment efficiency during acclimation.

Checks were made on the concentration of cyanide in the primary and final effluents. Following the acclimatization period, only traces of cyanide were present in the final effluents, even at the higher cyanide feed levels.

CONTINUOUS FEEDING

Copper Sulphate

Three concentrations of copper fed as copper sulphate were studied, 10, 15, and 25 milligrams per liter. Characteristics of the sewage feed during these runs are given in Table 13. BOD, COD, and suspended matter data for the final effluents of the copper fed units and the control are compared in Figures 8 and 9. The effluents of the units receiving copper fed as copper sulphate were predominantly of lower quality than those of the control units. The average percentage reductions in BOD and COD in treatment are shown in Table 14.

Table 13. AVERAGE CHARACTERISTICS OF SEWAGE TREATED IN COPPER SULPHATE STUDIES

Loading	Primary settler feed, mg/liter	Primary settler effluent, mg/liter
BOD	319	207
COD	513	363
Suspended matter	272	167

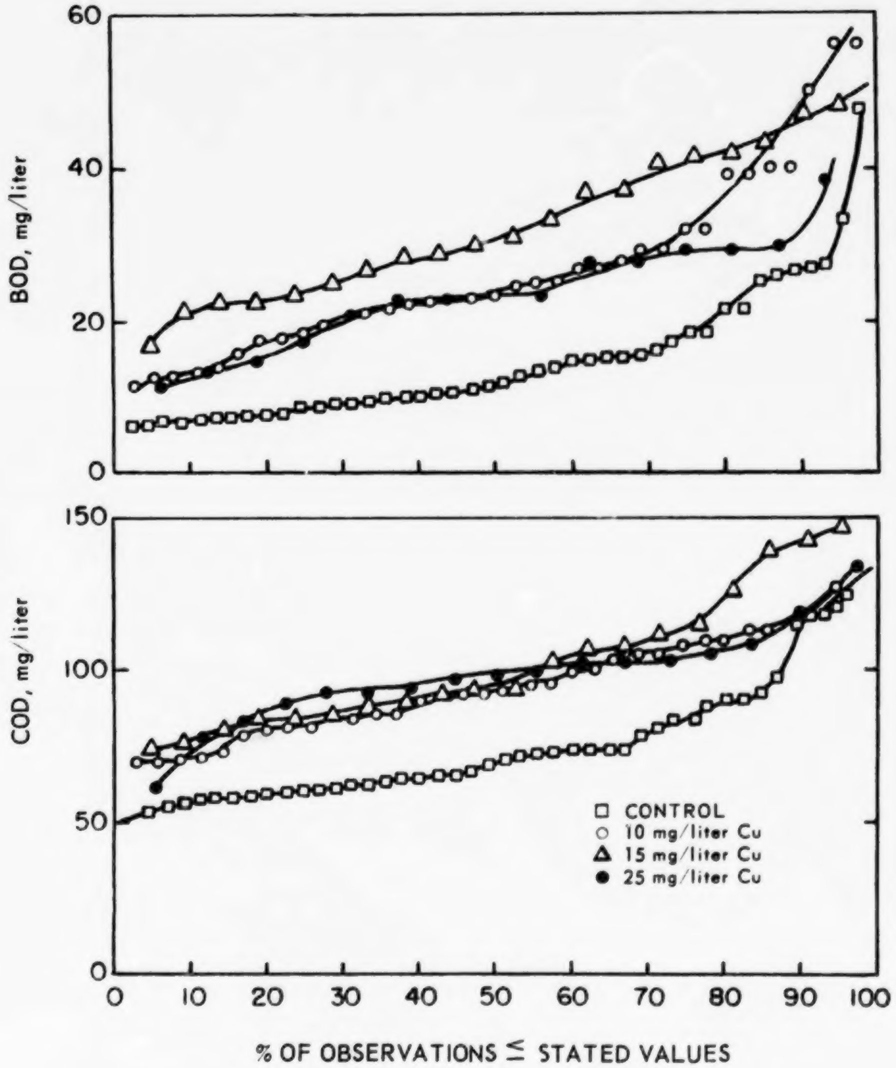

Figure 8. Effect of copper fed as copper sulphate continuously on BOD and COD of final effluents.

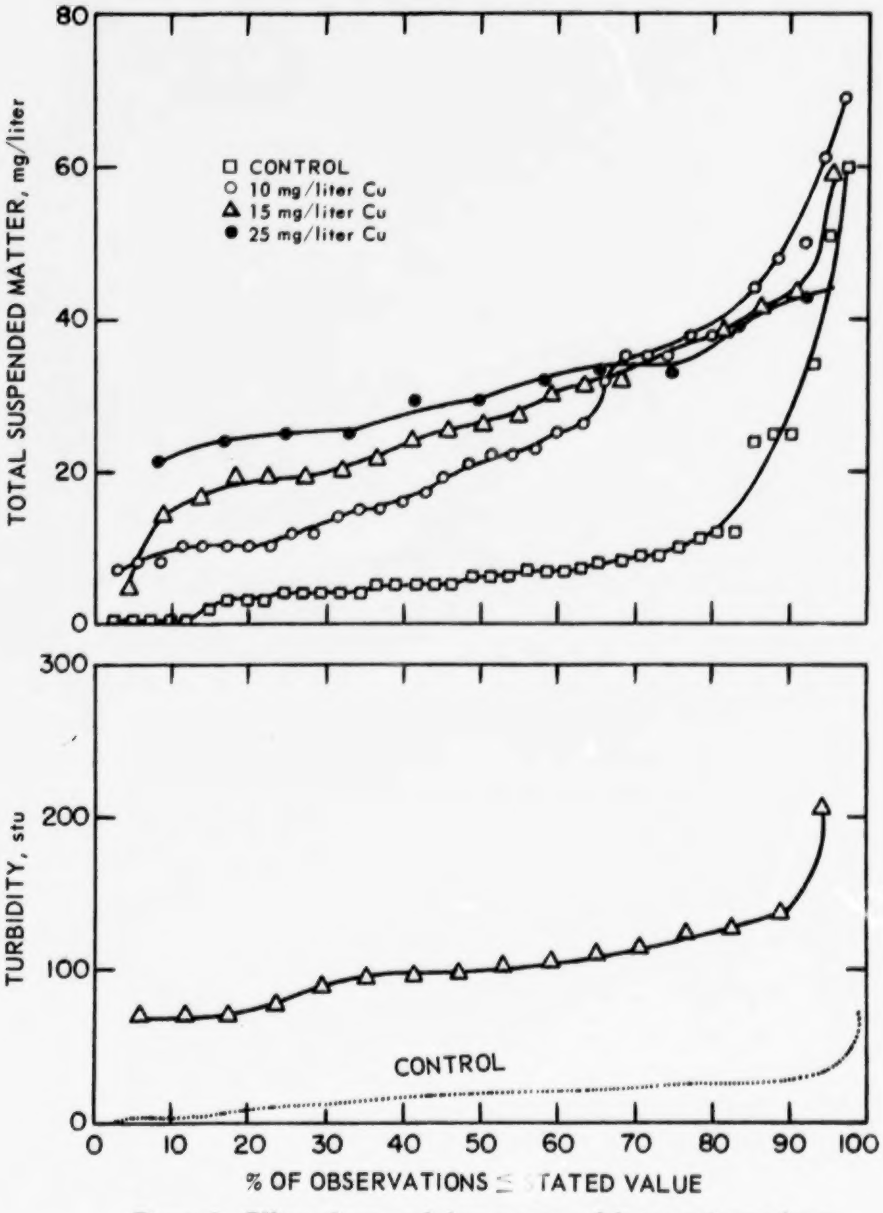

Figure 9. Effect of copper fed as copper sulphate continuously on suspended matter and turbidity of final effluents.

Table 14. EFFICIENCY OF ACTIVATED-SLUDGE TREATMENT OF SEWAGE CONTAINING COPPER SULPHATE, COPPER FED CONTINUOUSLY

Copper, mg/liter	Avg BOD removal, %	Avg COD removal, %
0	95.3	85.2
10	91.9	81.5
15	90.0	80.1
25	92.8	81.1

The ultimate disposition or fate in the treatment process of copper fed as copper sulphate during treatment is shown in Table

Table 15. FATE OF COPPER FED AS COPPER SULPHATE IN THE ACTIVATED-SLUDGE PROCESS

Type and location of check sample	Copper in sewage feed		
	10 mg/liter	15 mg/liter	25 mg/liter
Copper found in outlet			
Primary sludge, %	9	11	12
Excess activated sludge, %	55	58	51
Final effluent, %	21	21	21
Unaccounted for, %	15	10	16
Efficiency of copper removal, %	75	79	79
Soluble copper in primary effluent[a]			
Total, mg/liter	2.06	1.76	3.10
Reactive, mg/liter	1.12	1.06	1.96
Soluble copper in primary effluent[a]			
Total, mg/liter	0.53	2.32	1.27
Reactive, mg/liter	0.31	1.12	0.84

[a] Soluble copper is defined as that passing an HA45 Millipore membrane. Total soluble copper is that determined in the filtrate after acid digestion. Reactive soluble copper is that in filtrate which reacts with reagents in absence of prior digestion.

15. Information on the average efficiency of the activated-sludge process in removing copper fed as copper sulphate is included in Table 15. Soluble copper in the effluents is also shown. The concentrations of copper, both total and especially soluble, were highly variable among samples. In individual samples the concentration was as much as 100 percent greater than the mean.

Cyanide Complex

Five concentrations of copper fed as copper cyanide complex were studied, 0.4, 1.2, 2.5, 5, and 10 milligrams per liter. Characteristics of the sewage feed during these runs are given in Table

Table 16. AVERAGE CHARACTERISTICS OF SEWAGE TREATED IN COPPER CYANIDE COMPLEX STUDIES

Loadings	Primary settler feed, mg/liter	Primary settler effluent, mg/liter
BOD	269	207
COD	460	318
Suspended matter	306	162

16. BOD, COD, suspended matter, and turbidity data for the final effluents of the copper fed units and the control are compared in Figures 10 and 11. The average percentage reductions in BOD and COD in treatment are shown in Table 17.

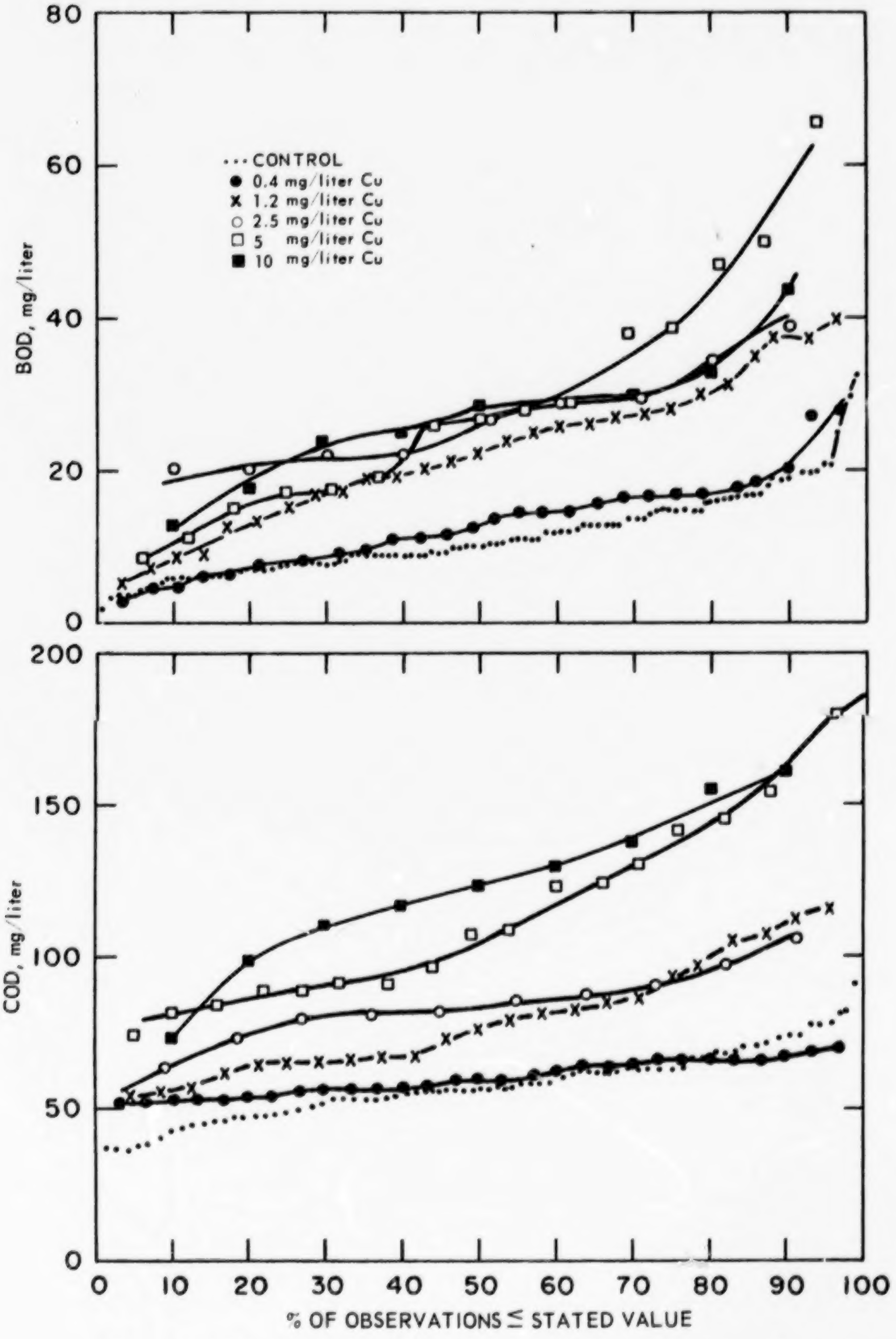

Figure 10. Effect of copper fed as copper cyanide complex continuously on BOD and COD of final effluents.

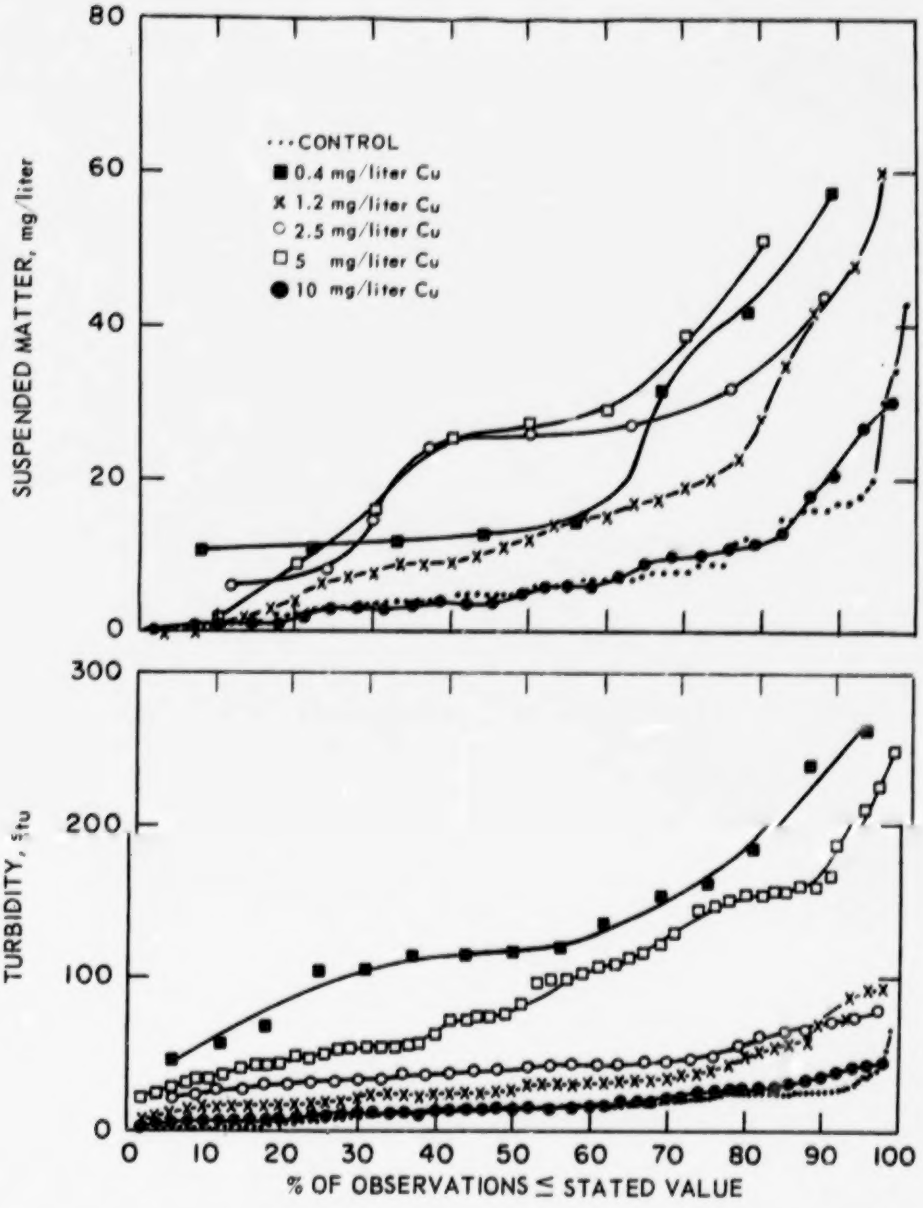

Figure 11. Effect of copper fed as copper cyanide complex continuously on total suspended matter and turbidity of final effluents.

Table 17. EFFICIENCY OF ACTIVATED SLUDGE TREATMENT OF SEWAGE CONTAINING COPPER CYANIDE COMPLEX, COPPER FED CONTINUOUSLY

Copper, mg/liter	Avg BOD removal, %	Avg COD removal, %
0	95	85
0.4	95	85
1.2	93	84
2.5	91	85
5	89	76
10	88	69

The BOD, COD, suspended matter, and turbidity data for the final effluents of the units receiving 0.4 and 1.2 milligrams per liter copper and the control were subject to statistical analysis. At the 0.4-milligram-per-liter copper level the differences between the metal fed unit and the control were not statistically significant. At 1.2 milligrams per liter of copper, all parameters differed significantly, that is, the likelihood that the differences were due to chance alone is very low. The data are plotted on logarithmic probability distribution paper in Figure 12.

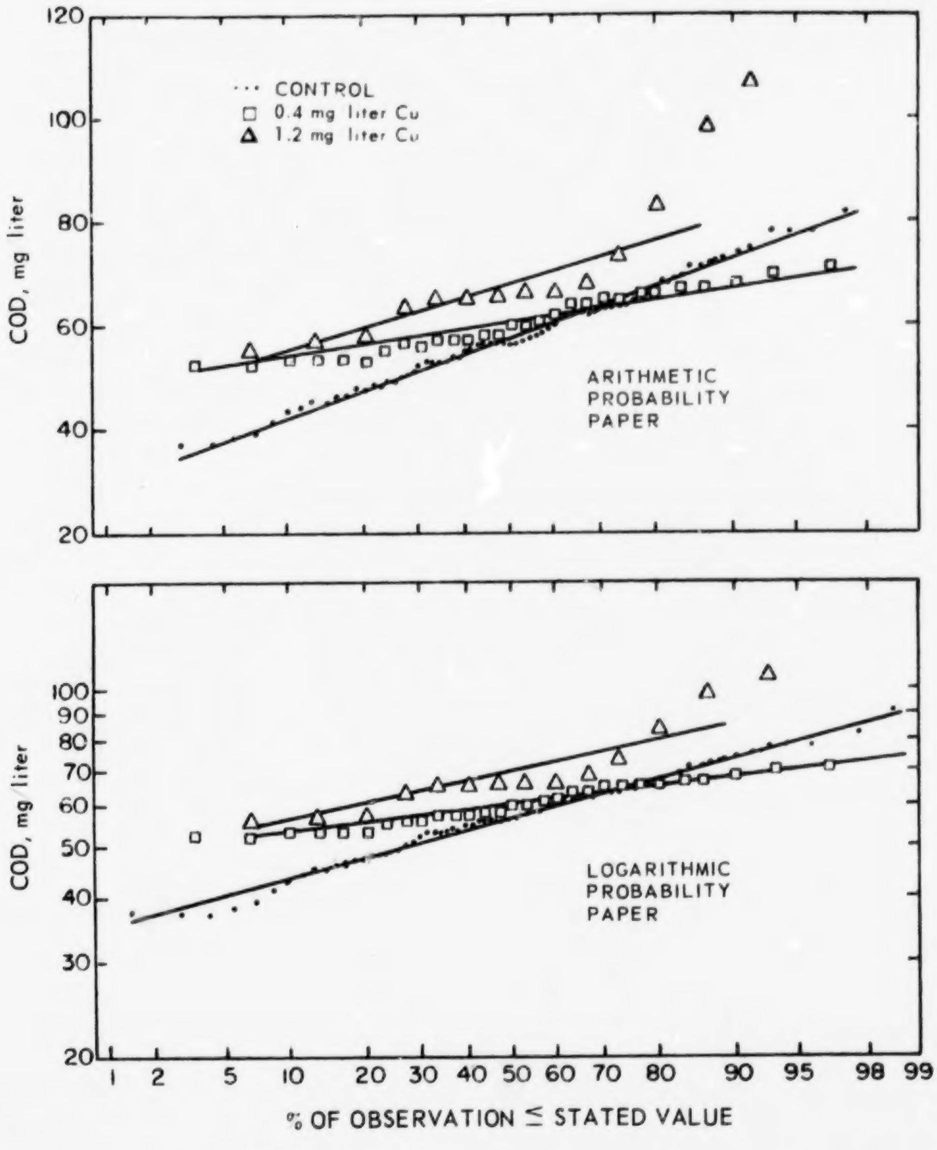

Figure 12. Effect of copper fed as copper cyanide complex continuously on COD of final effluents.

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The ultimate disposition or fate in the treatment process of copper fed as copper cyanide complex during treatment is shown in Table 18. The average efficiency of the activated-sludge process in removing copper fed in the cyanide complex form is included in Table 18 as well as copper in solution in the effluents. The quantity of copper in solution was highly variable among samples for each series.

Table 18. FATE OF COPPER FED AS COPPER CYANIDE COMPLEX IN ACTIVATED-SLUDGE TREATMENT

Type and location of check sample	Copper in sewage feed			
	0.4 mg/liter	1.2 mg/liter	2.5 mg/liter	5 mg/liter
Copper fed found in outlet				
Primary sludge, %	–	12.5	10.7	7
Excess activated sludge, %	–	43.3	25.6	23
Final effluent, %	43	25.1	43.3	50
Unaccounted for, %	–	20	20	20
Efficiency of copper removal, %	57	75	57	50
Soluble copper in primary effluent				
Total, mg/liter	0.22	0.19	–	–
Reactive, mg/liter	–	–	–	2.65
Soluble copper in final effluent				
Total, mg/liter	0.12	0.10	–	–
Reactive, mg/liter	–	–	0.67	0.92

The relationship between plant load and the effect of copper was studied during a short period of operation of the pilot plants at about double normal plant loadings.

Copper was fed as copper cyanide complex at 10 milligrams per liter for this experiment. The data obtained are shown in Table 19.

Table 19. RELATIONSHIP BETWEEN PLANT LOAD AND THE EFFECT OF COPPER FED AS COPPER CYANIDE COMPLEX[a]

Pilot plant	Plant loading, BOD		Final effluent quality[b]			
	lb/1,000 ft^3 aerator capacity, avg	lb/day/lb VS under aeration, avg	BOD, mg/liter	BOD, mg/liter	Suspended matter, mg/liter	Turbidity, stu[c]
A.						
Control	48	0.56	11	69	6	17
Copper fed	48	0.56	23	98	29	100
B:						
Control	100	1.37	19	82	20	23
Copper fed	119	0.98	33	130	32	71

[a] 10 mg/l fed continuously

[b] Median values.

[c] stu indicates standard turbidity units

The increased plant loadings were obtained by doubling the sewage feed rate; detention times, therefore, were half the values listed in Table 12. The characteristics of the sewage during this special experiment were about the same as those listed in Table 16.

The normal experimental run with 10 milligrams per liter of copper fed as the copper cyanide complex was followed by a special investigation of the effects of cyanide alone. A substitution of sodium cyanide was made for the copper cyanide in the sewage feed. The quantity of sodium cyanide added was sufficient to make the concentration of cyanide in the sewage the same as that when the metal complex mixture was fed, a concentration of 12.5 milligrams per liter as CN^-. After a few days the quality of the effluent improved until it was not significantly different from that of the control.

A direct comparison was made between the effect on acclimated systems of 1.2 milligrams per liter copper fed as copper sulphate and the same copper concentration fed as copper cyanide complex. This comparison was made with parallel operation of two units fed copper and a control unit so that the sewage fed to each unit and environmental factors were as alike as reasonably achievable. There were no significant differences in the quality of the effluents from the two copper-fed units.

Information on the acclimation or adaption phenomena of activated sludge is given in Figure 13. Activated sludge with no history of having received copper-bearing wastes was used for the studies of continuous feeding of CuCN and $CuSO_4$ at 1.2 milligrams per liter. The COD of daily composite samples of the final effluents of these units is shown in Figure 13 for several days immediately after the metal dose was started. Also, the quality of the final effluent immediately following an increase from 2.5 to 10 milligrams per liter of copper fed as copper cyanide complex is shown.

Microscopic examinations of the activated sludge were made occasionally for general appearance of the sludge and presence of protozoa and rotifera. Protozoa and rotifera were absent during the acclimation period for many of the runs, but even at the 5-milligram per-liter level of copper a normal population density of the higher forms eventually was present. The appearance of sludge from a unit receiving 1.2 milligrams per liter copper and greater, differed from that of sludge in the control unit; it was characterized by dense small sludge particles. The sludge from the copper-fed units settled rapidly. The sludge density index for the activated sludge obtained during the 0.4-milligram-per-liter copper run averaged 1.4 and that during the 1.2-milligram-per-liter copper run averaged 1.3. The copper-fed unit never was troubled with settling problems caused by filamentous forms, although filamentous bulking was a frequent problem in the control unit.

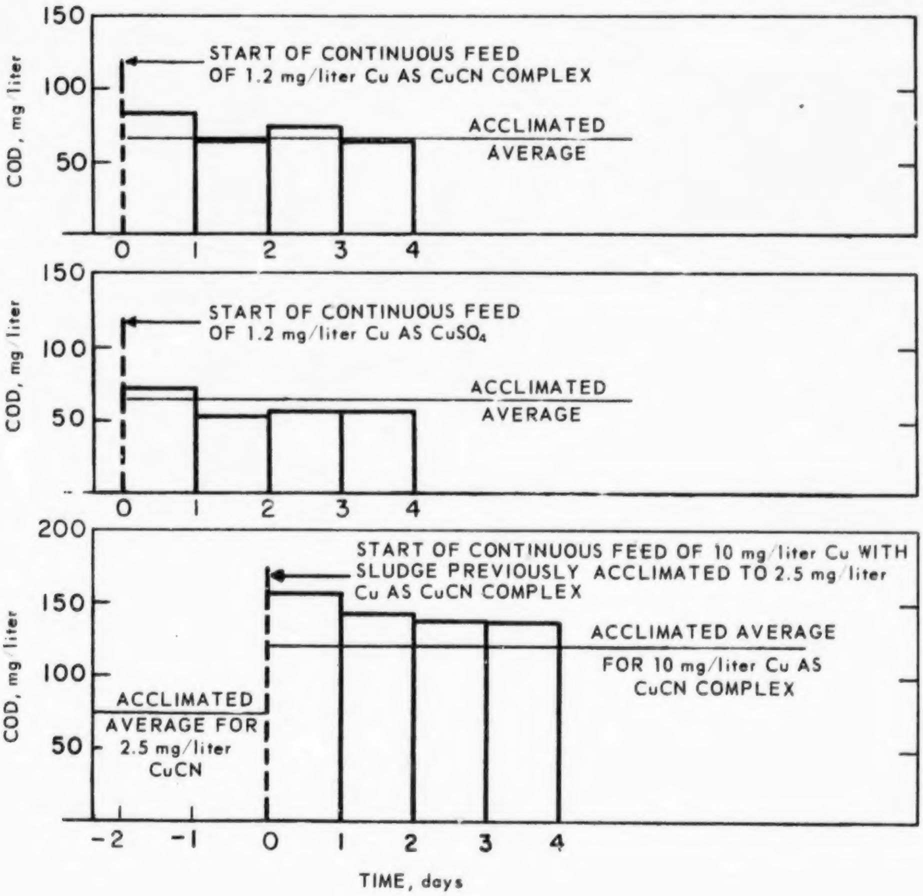


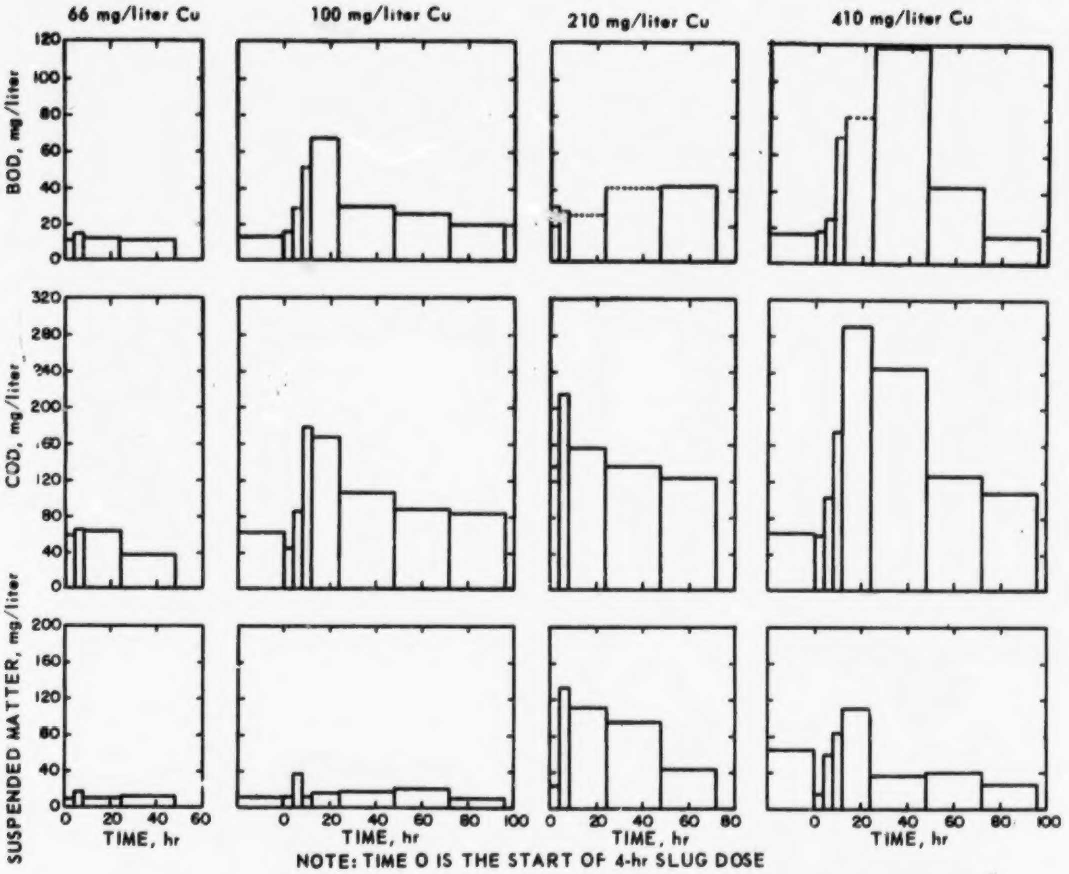
Figure 13. COD of final effluents during acclimation to copper.

SLUG DOSES

Copper Sulphate

The effects of four slug doses of copper fed as copper sulphate on the activated-sludge process were studied. Sludge with no history of having previously received copper was used. The effects of the four doses on BOD, COD, and suspended matter content of the final effluents are shown in Figure 14. The sewage feed during these runs had an average BOD of 264 milligrams per liter and an average COD of 407 milligrams per liter.

The fate of the copper fed at 100 milligrams per liter is shown in Figure 15. The primary sludge withdrawn 7 hours after start of of the slug dose contained 31 percent of the copper fed. Material balances in copper fed to and discharged from the primary settler in the 24 hours after start of the slug accounted for 93 percent of the copper fed. The aerator liquor solids contained a maximum of copper 8 hours after the beginning of the slug, at which time 46 percent of



NOTE: TIME 0 IS THE START OF 4-hr SLUG DOSE

Figure 14. Effect of slug doses of copper fed as copper sulphate on the BOD, COD, and suspended matter of final effluents.

the copper fed was associated with the solids in the aerator. At 96 hours the copper in the aerator solids had decreased to 20 percent of that fed. Copper was slowly released from the aerator and appeared in the final effluent.

Overall material balances including accumulation of copper in the aerator accounted for about 75 to 80 percent of the copper at seven sampling times during the 96-hour run. The cumulative quantity of copper discharged in the final effluent during the 96 hours following slugging was 20 percent of the copper fed. Because 20 percent of the copper fed was associated with the aerator sludge at that time and the concentration in the final effluent had dropped to low levels, the process is about 75 percent effective in removing copper as copper sulphate fed in a slug dose of this magnitude. The copper removed was associated with the primary and excess activated sludges.

The fate of copper at a slug feed level of 410 milligrams per liter is shown in Figure 16. The primary sludge withdrawn 7.5 hours hours after the start of the slug contained 15 percent of the copper fed. Material balances in copper fed to and discharged from the

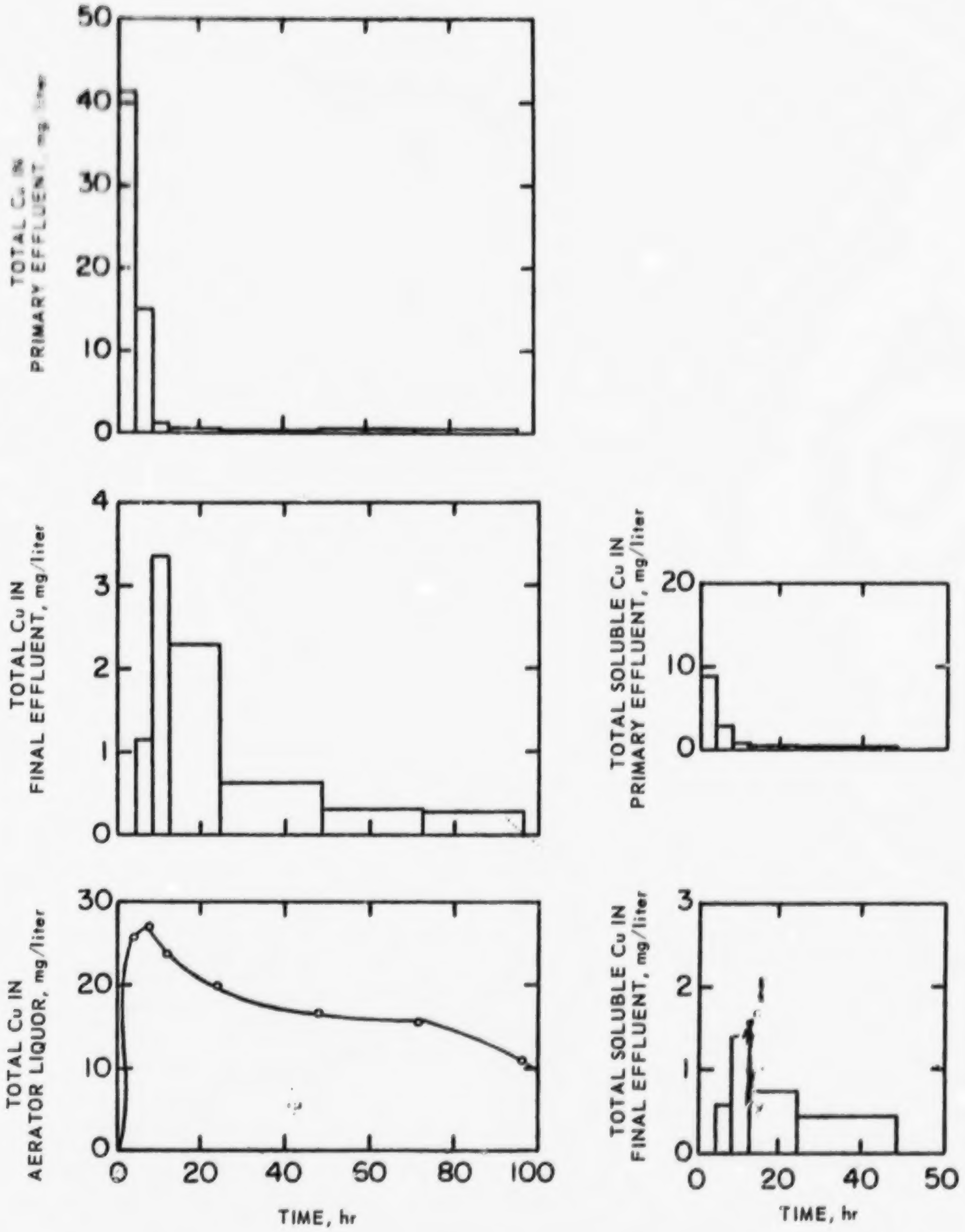


Figure 15. Fate of copper in activated-sludge treatment, slug dose of 100 mg/liter fed as copper sulfate.

primary settler in the 24 hours after start of dosing accounted for 83 percent of the copper fed. Much of the copper was adsorbed on the biological floc in the aerator. Twelve hours after start of the slug about 50 percent of the copper fed was in the aerator. This copper was predominantly associated with the biological sludge. The sorbed copper was slowly released to the final effluent resulting in an extended period during which copper at relatively low levels was in the final effluent. Overall material balances 24 hours after start

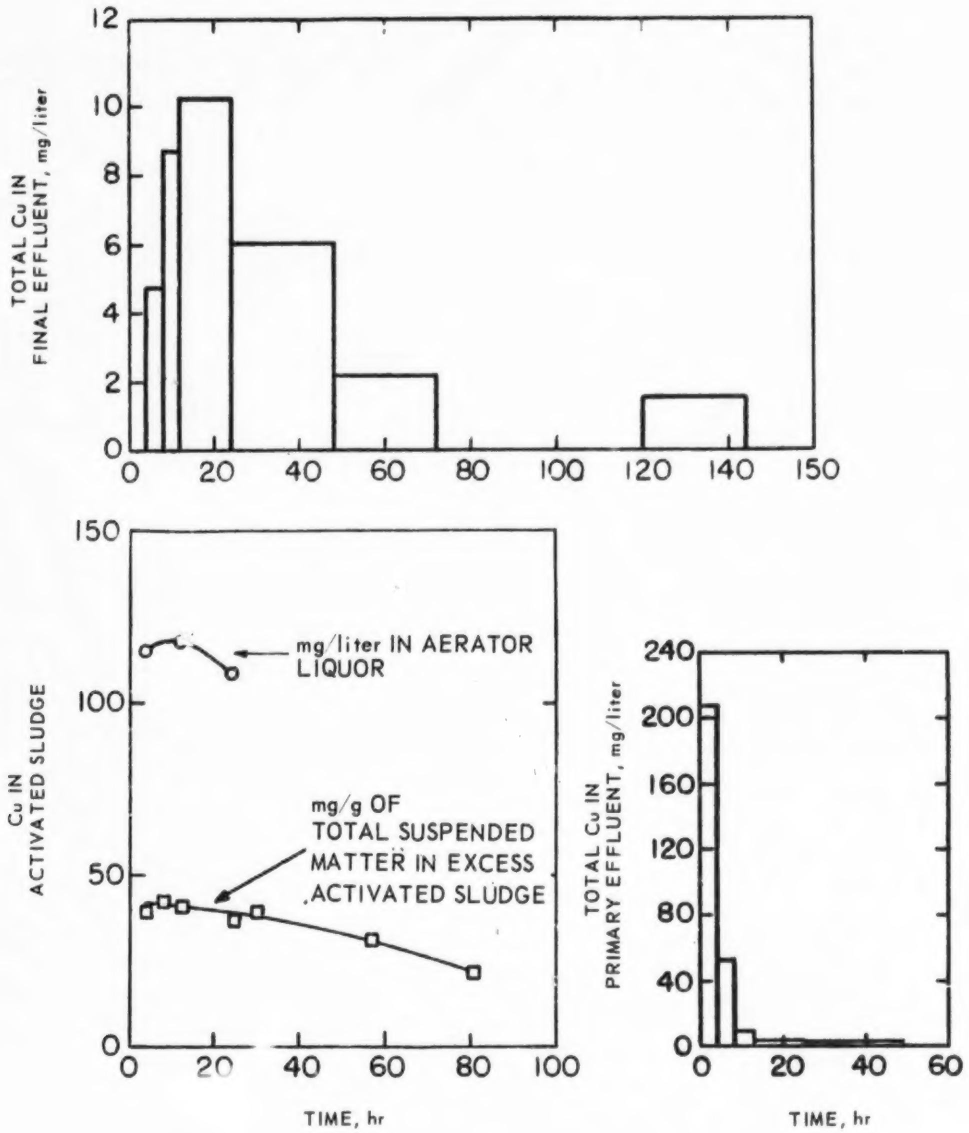


Figure 16. Fate of copper in activated-sludge treatment, slug dose of 410 mg/liter fed as copper sulfate.

of the slug dose, including accumulation of copper in the aerator, accounted for 75 percent of the copper.

Three grab samples taken from the final effluent during the high copper concentration periods showed that an average of 61 percent of the copper discharged in the final effluent was in solution. The cumulative quantity of copper discharged in the final effluent during the 96-hour period following the start of the slug was 23 percent of the copper fed. The process is estimated to be about 65 percent effective in removing a slug dose of copper of this magnitude.

Cyanide Complex

The effects of three slug doses of copper fed as copper cyanide complex were studied. The effects of the three doses on BOD, COD, suspended matter, and turbidity of the final effluents from the activated-sludge process are shown in Figure 17. The sewage feed during these runs had an average BOD of 258 milligrams per liter and an average COD of 380 milligrams per liter. Two of these slug doses were made into activated sludges that had continuously received a 0.4-milligram-per-liter concentration of copper fed as the copper cyanide complex for several weeks preceding the slug test.

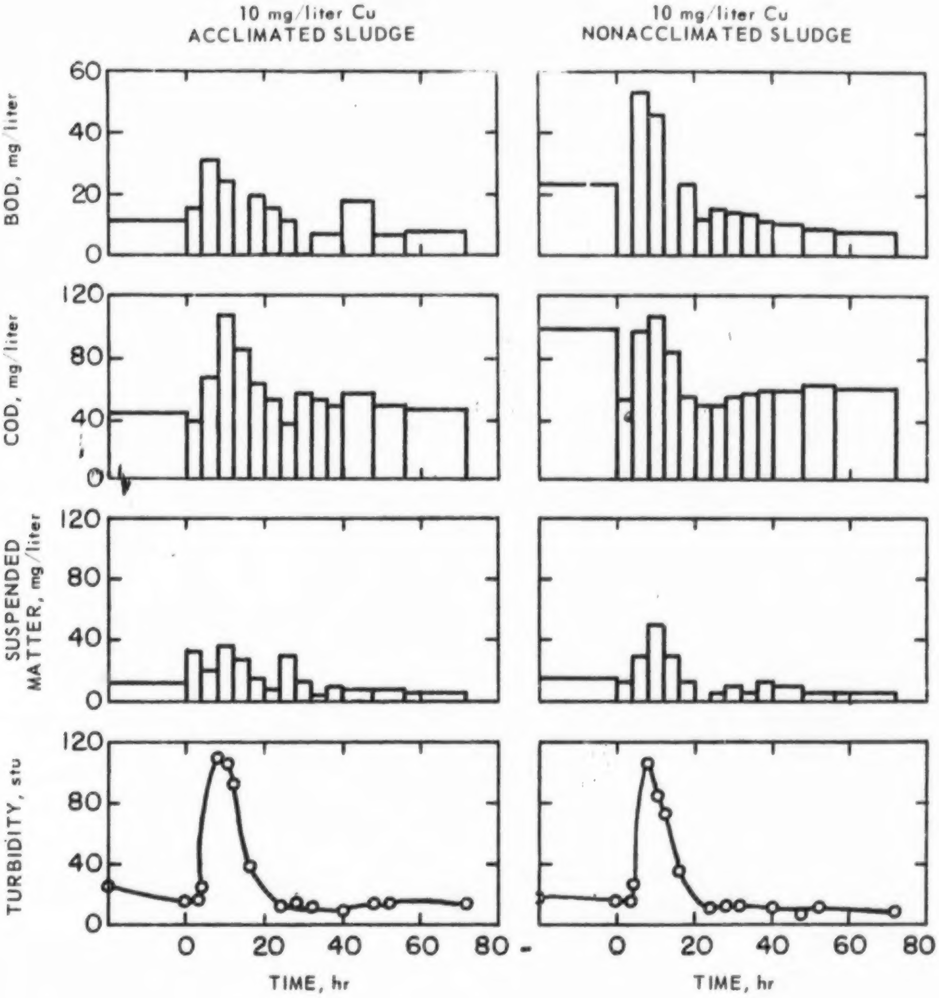


Figure 17. Effect of slug doses of copper fed as copper cyanide complex on BOD, COD, suspended matter, and turbidity final effluents.

The maximum copper content of the primary effluent was about equal to the dose concentration in each of three runs, and practically all of this copper was in solution. A negligible part of the copper was removed in primary settling.

Data on the copper concentrations in grab samples of final effluents are shown in Figure 18. A great part of the copper passed through the process and remained almost entirely in soluble form. The efficiency of the process in removing copper was not greater than 25 percent.

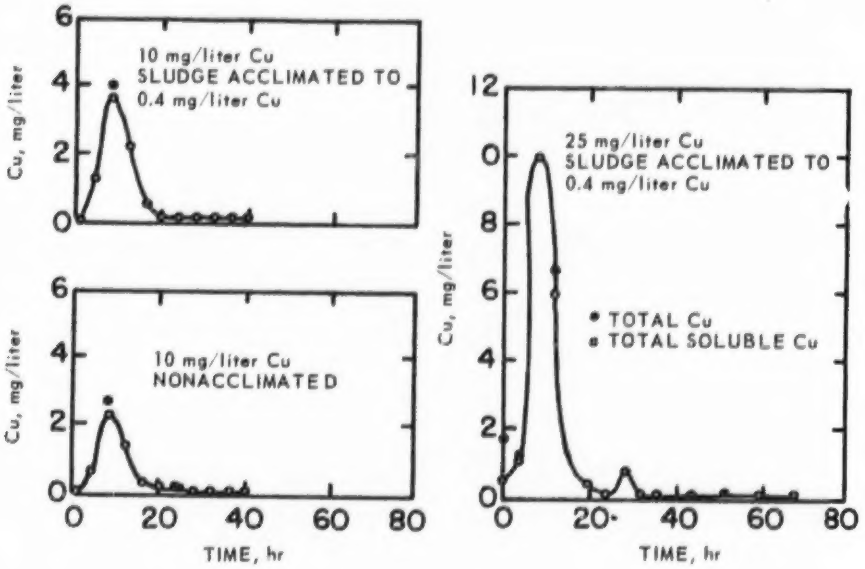


Figure 18. Copper in final effluent following slug doses of copper fed as copper cyanide complex.

DISCUSSION OF RESULTS

Reductions in treatment efficiency caused by copper fed as copper sulphate at concentrations of 10, 15, and 25 milligrams per liter were unexpectedly low. The reduction in efficiency averaged 4 percent or less. The data for each of the concentrations were much alike. In fact, in some cases average reductions in treatment efficiency were in reverse order of the copper concentrations. Initial observations led us to think that copper cyanide complex had a much greater effect than copper sulphate, but the effects proved to be significantly different only for the acclimation or adaption period, as discussed later. Reductions in efficiency of similar magnitude prevailed at copper concentrations from 25 milligrams per liter down to and including 2.5 milligrams per liter. The direct comparison of the effects of the two forms, the sulphate and cyanide complex, in a parallel run at copper concentrations of 1.2 milligrams per liter showed no significant difference in the effects.

The use of turbidity as a measure of effluent quality was initiated after the project was partially completed, when it became obvious that marked differences in turbidity were occurring, as shown in Figures 10 and 11. The differences between turbidities of the control and copper-fed units were greater and more consistent than any other measurement. Increased turbidity occurred with increased copper concentration.

The change in efficiency with copper level was so gradual that a large number of observations and statistical definition of differences would be needed for bracketing the tolerance level to within 0.1 milligram. Copper may have an effect down to trace levels, but the accuracy of measurement and sampling errors limit measurement of the effect at very low levels. Small reductions in treatment efficiency have little practical meaning because of limited accuracy in estimation of damaging effects on receiving waters. A permissible limit for protection of aerobic treatment efficiency can be established appropriately, with little caution, since at high concentrations only about 7 percent reduction in BOD efficiency is indicated. The maximum concentration of copper that can be received continuously in normal domestic sewage without having a detectable effect on common parameters of effluent quality is 1 milligram per liter. Where turbidity is used as a treatment criterion, a maximum copper concentration of about 0.8 milligram per liter appears to be necessary to obtain an effluent that is not significantly affected.

The activated-sludge process averaged from 50 to 79 percent efficient in the removal of copper over the concentration range from 0.4 to 25 milligrams per liter based on analyses of the final effluents. Some 30 to 50 percent of the copper passing through the process was in soluble form. All the copper in soluble form in the final effluent would not react with the analytical reagent directly. Digestion of the filtrate preceding analysis consistently showed more copper. This indicated that either complexes or colloidal copper passed through the Millipore membrane. Where the cyanide complex was being fed, it might have been anticipated that some of the soluble copper in the final effluent would be cyanide complexes. The cyanide determination, however, showed only traces of cyanide, and furthermore, considerable unreactive filterable copper was present in the effluents when the copper was fed as copper sulphate.

At the 1-milligram-per-liter level of copper, the protozoa and rotifera were present in normal numbers. The sludge settles rapidly; in fact, it appears that sufficient concentration of copper will prevent the growth of filamentous organisms responsible for certain types of sludge bulking.

Copper fed as copper sulphate in a slug dose of 4 hours duration at a concentration of 66 milligrams per liter in the sewage had but slight effect on the BOD, COD, or suspended matter content of the final effluent. The 100-, 210-, and 410-milligram-per-liter doses of copper as copper sulphate caused severe effects over the first 48 hours, somewhat in proportion to the copper dose. With the 100-milligram-per-liter dose, efficiency of BOD removal fell off to about 50 percent and normal operation was restored in about 120 hours. Even with doses as large as 410 milligrams per liter, the sludge was not destroyed but recovered to normal in about 100 hours.

Slug doses of copper fed as copper cyanide complex had a much more severe effect than the other slug doses at the same concentration. The maximum COD and BOD of the effluent from units fed copper as the copper cyanide complex at 10 milligrams per liter were almost as high as when copper was fed as copper sulphate at 100 milligrams per liter. The duration of the damages from the complexed metal fed at the 10-milligram-per-liter level was about 24 hours. This damage period is only one-fourth the period that resulted from the copper sulphate doses. A slug of copper fed as the copper cyanide complex at 25 milligrams per liter resulted in a very severe upset of the plant. The COD of the effluent for one 4-hour period was considerably greater than that of the feed. The duration of the effect was also about 24 hours. The cyanide portion of the complex is apparently much more toxic than the metal, or perhaps the important factor is that cyanide keeps the metal in solution. When the amounts of metal in solution are compared, it is seen that with the 100-milligram-per-liter copper sulphate slug, copper was present in the final effluent at a maximum of only 3 milligrams per liter; whereas with a 25-milligram-per-liter dose of copper cyanide complex, soluble copper was present in the final effluent at 10 milligrams per liter.

An explanation of the more prolonged effect of the copper sulphate slug is found in the observation that the copper in the copper sulphate was adsorbed by the sludge and retained in the unit for an extended period. The copper in the cyanide complex, on the other hand, was apparently not adsorbed to any appreciable extent and was carried through the unit rapidly.

Once the biological system has become acclimated to the copper and cyanide, and adapted to degradation of the cyanide radical, differences in effects between the two forms of copper disappear. This accounts for the similar effects the two forms have in acclimated systems.

Acclimation to a low copper cyanide level, 0.4 milligram per liter, had no value in reducing the effect of a 10-milligram-per-liter slug dose.

Massive slug doses are necessary to eliminate the higher organisms from the sludge.

Slug observations indicate that slugs of 4-hour duration and with up to 10-milligram-per-liter concentrations of copper as copper cyanide complex or up to 50-milligram-per-liter concentrations of copper as copper sulphate have a minor effect on efficiency and the effect is not prolonged.

ANAEROBIC SLUDGE DIGESTION*

The digestion of copper-bearing sludges was studied by operation of bench-scale sludge digesters on sludge feeds obtained from pilot activated-sludge plants. Sewage from a common source was fed to three replicate activated-sludge plants. Copper solutions were introduced continuously to the feed of certain pilot plants to produce selected constant concentrations. One plant was operated in parallel with no metal addition to the feed. Sludge from this plant was fed to digesters that served as controls. Differences in gas production between the control digesters and those receiving copper-bearing sludges were attributed to the presence of copper in the sludge.

The first part of this chapter, presenting the findings of an investigation of the effects of copper on the activated-sludge sewage treatment process, contained information on the sewage feed (13).

Procedure

The sludge digesters were 5-gallon glass carboys, which were fitted with pumps for mixing the digester contents (Figure 19.) The pump-mixing arrangement was superior to hand shaking in obtaining representative samples and waste sludge. The digesters were maintained at 30° C in a constant-temperature room. Gas was collected in a floating-cover gas holder, and the volume was measured daily at atmospheric pressure and at 30° C.

Primary sludge for digester feeds was withdrawn once each day from the pilot plant primary settler. The withdrawn sludge was settled for 30 minutes and supernatant decanted. This settled sludge usually contained about 2 percent total suspended matter. The excess activated sludge to be fed the digesters was withdrawn from the secondary settler once each day and fed to the digester without delay. The total suspended matter in the secondary sludge digester feed was 0.5 percent or less.

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*Remainder of this chapter published previously in *Journal Water Pollution Control Federation.* Washington, D. C. 20016. See Reference 18.

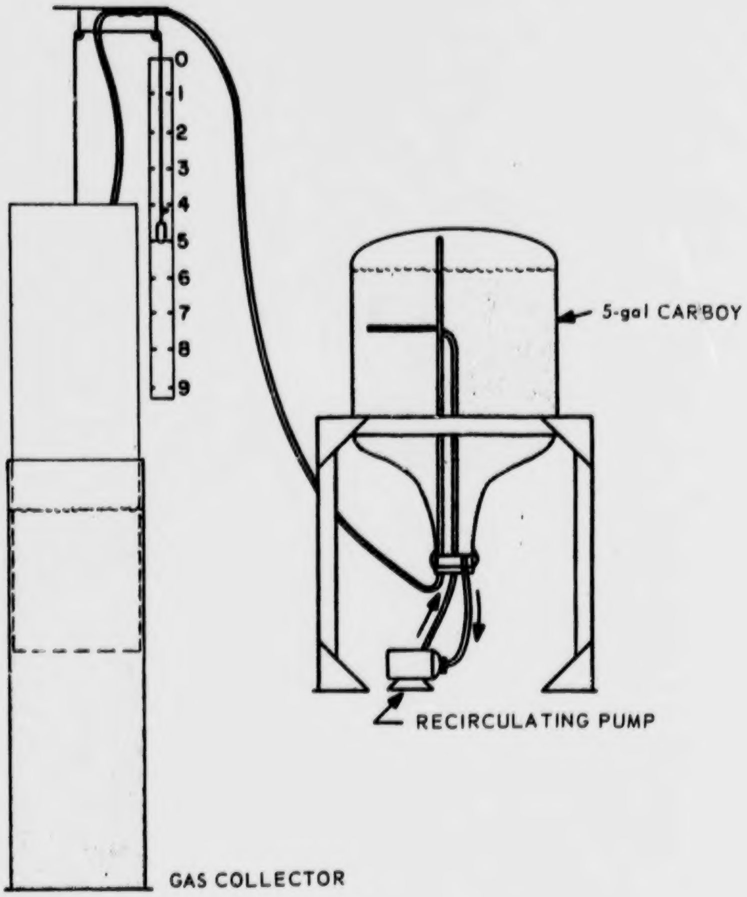

Figure 19. Experimental digester and gas collection apparatus.

A volume of 470 milliliters of mixed digester contents was removed once each day from the digester receiving primary sludge only. An equal volume of primary sludge was then fed. A volume of 8 liters was maintained in the digester, which corresponds to a detention period of 17 days. The 470 milliliters of feed contained about 10 grams of volatile matter.

The digesters receiving combined primary and excess activated sludges were fed 300 milliliters of primary sludge and 700 milliliters of excess activated sludge each day. The two sludge volumes provided a total of about 10 grams of volatile suspended matter, about 35 percent of which was contained in the excess activated sludge. This is approximately the same relationship of primary and excess activated sludge as was produced in the pilot plants. A sludge volume of 16 liters was maintained in the digesters receiving the combined sludges, which corresponds to a detention period of 16 days. One liter of mixed digester contents was removed once each day and replaced with the feed sludges. Digester loading information is summarized in Table 20.

Table 20. LOADING FACTORS FOR DIGESTERS

Item	Primary sludge digester	Primary and excess activated-sludge digester
Capacity, liters	8	16
Detention (days)	17	16
Loading, lb VS/day/ 1,000 ft^3 of digester volume.	78	39

The digesters were seeded originally with sludge from a municipal sewage treatment plant. The digesters were fed for a week or more with sludges from the activated-sludge plant, which had received no addition of copper to its feed before the feeding of copper-bearing sludge was started.

A sample of each digester feed and digested sludge withdrawn was collected each day. These daily samples were composited for weekly periods and analyzed for copper and for total suspended and volatile suspended matter. Gas production on a per-unit-of-volatile-solids basis was computed on a weekly basis, with gas production lagging the feed compositing period by 1 day.

Since the digester was completely mixed when wasting sludge, the accumulation of copper in the digester would follow the principles of displacement of one material, A, from a homogeneously mixed system by continuous addition of a second material, B. Accordingly, after a period of time equal to the digester volume divided by daily feed volume (one detention period), the sludge of the new origin (copper-bearing) would constitute just over 60 percent of the sludge in the digester. After four periods only a negligible percent of the original sludge would be left. For this reason the digesters were operated for over 60 days before an experiment was terminated.

Results

Some data on common digester parameters, such as pH, alkalinity, volatile acids, and gas composition, were obtained. All such measurements were not routinely made, however, since it was considered that they would be symptoms of a damaging effect of copper that would ultimately be reflected in gas production data. In no case were liming or out-of-the-ordinary steps taken to correct any abnormal performance condition.

High concentrations of copper were measured by the usual iodimetric titration after complexing iron present with ammonium bifluoride; low concentrations were determined by the colorimetric cuprethol method. The organic matter was destroyed by fuming with sulfuric and nitric acid. For determining soluble copper, the sample was passed through an HA45 Millipore membrane. Copper in some forms will pass through the membrane filter, but will not react with cuprethol. Digestion to destroy complexes is necessary to determine total soluble copper in such samples. Colloidal copper in sizes that pass the membrane filter could have been present. Copper in the filtrate that reacts with cuprethol without digestion is termed reactive soluble copper in this paper.

Copper was fed to the sewage in two forms, i.e., copper sulfate and copper cyanide complex, $Na_nCu(CN)_n$. Restrictions are usually placed on the discharge of wastes containing cyanides to sewerage systems, because of potential hazards through release of HCN. These restrictions limit the cyanide to low levels so that experimentation at higher cyanide levels would not ordinarily be of practical value. In the case of the copper cyanide complex, there is the possibility that the cyanide *per se* could affect the anaerobic organisms or that the cyanide in combination with the copper would have a synergistic effect. It has been previously reported that 16 milligrams per liter of cyanide fed as sodium cyanide has no effect on sludge digestion after an acclimation period (14). This concentration is greater than maximum concentration of cyanide used in these sludge digestion studies.

Gas production from digestion of primary sludges obtained from sewage containing 10, 15, and 25 milligrams per liter of copper are shown in Figures 20, 21, and 22. Gas production from digestion of combined primary and excess activated sludges from sewage fed 5, 10, 15, and 25 milligrams per liter of copper is shown in Figures 23, 24, 25, and 26. The graphs include observations of digesters fed copper as copper cyanide complex and as copper sulfate, as designated in the titles.

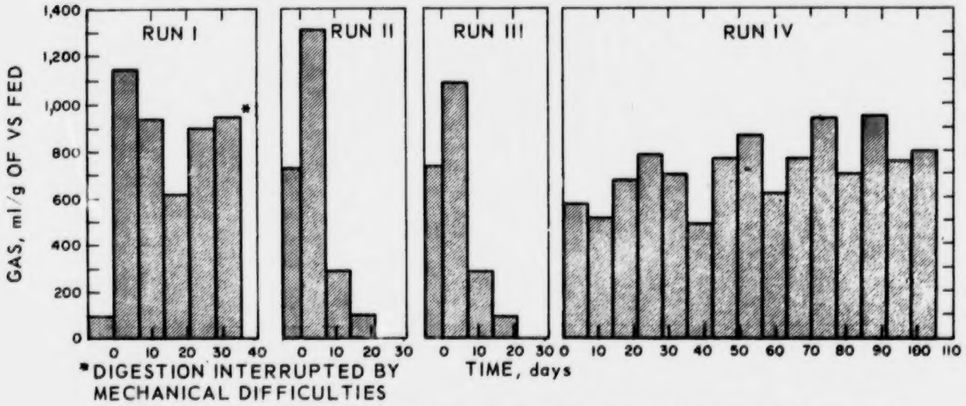

Figure 20. Performance of digester fed primary sludges from unit receiving 10 mg/liter copper fed as copper cyanide complex.

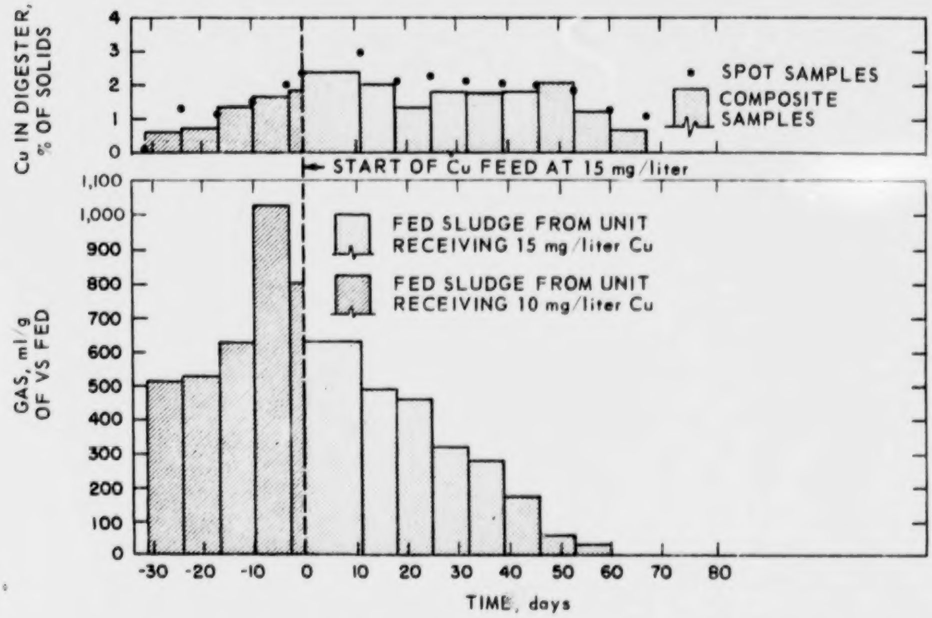

Figure 21. Performance of digester fed primary sludge from unit receiving 15 mg/liter copper, fed as copper sulfate.

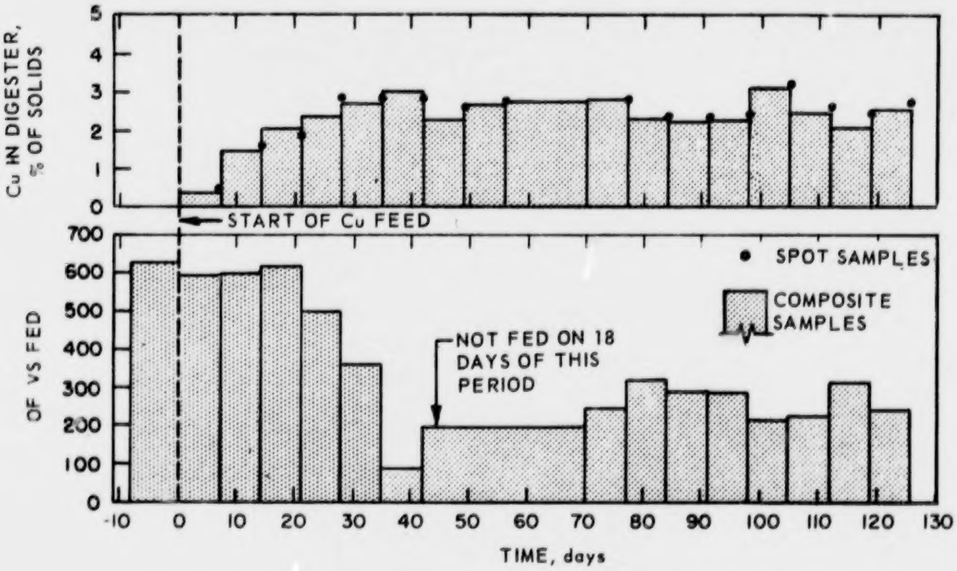

Figure 22. Performance of digester fed primary sludge from unit receiving 25 mg/liter copper, fed as copper sulfate.

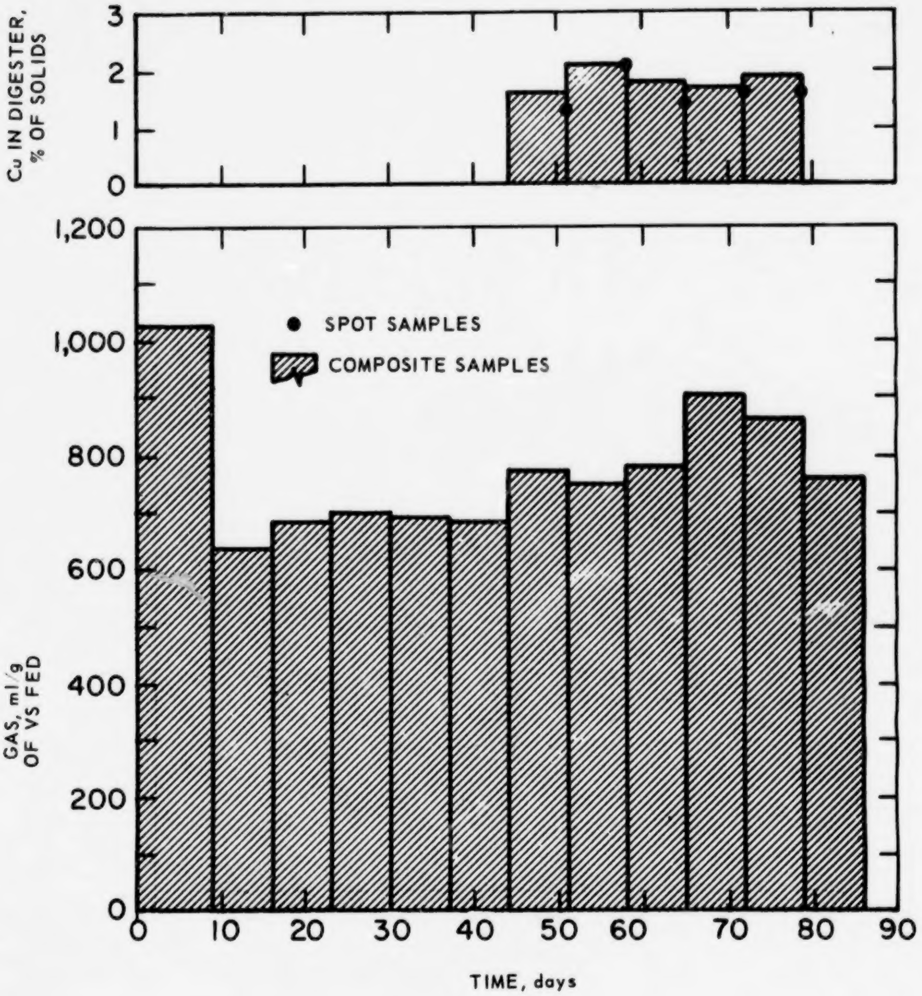

Figure 23. Performance of digester fed combined sludges from unit receiving 5 mg/liter copper, fed as copper cyanide complex.

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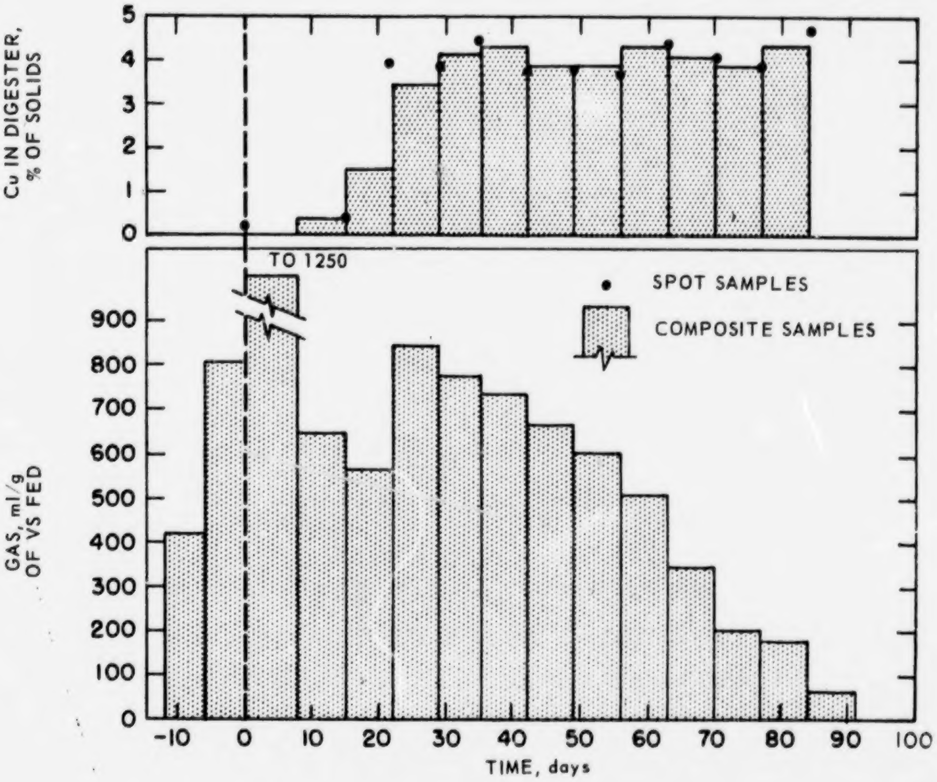

Figure 24. Performance of digester fed combined sludges from unit receiving 10 mg/liter copper, fed as copper sulfate.

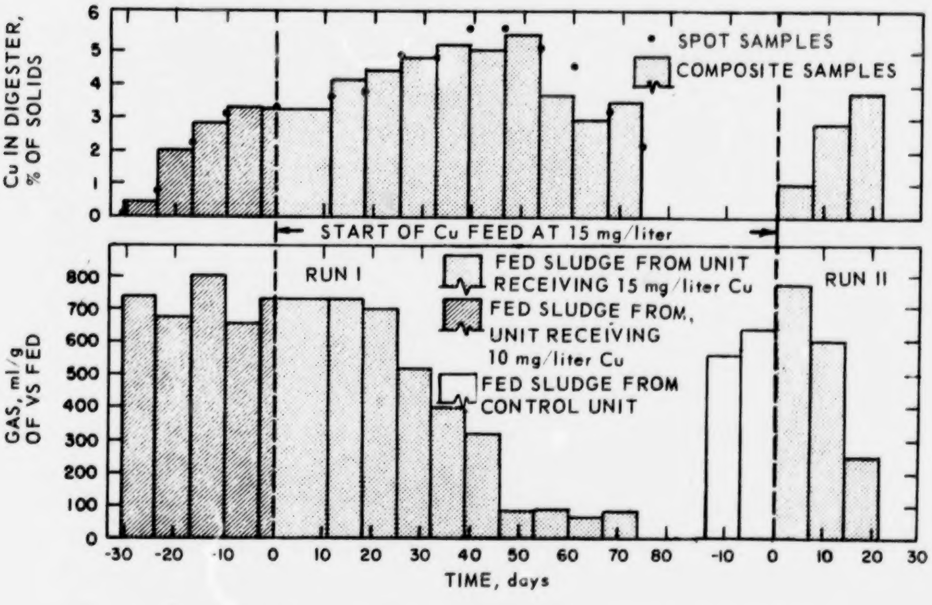

Figure 25. Performance of digester fed combined sludges from unit receiving 15 mg/liter copper, fed as copper sulfate.

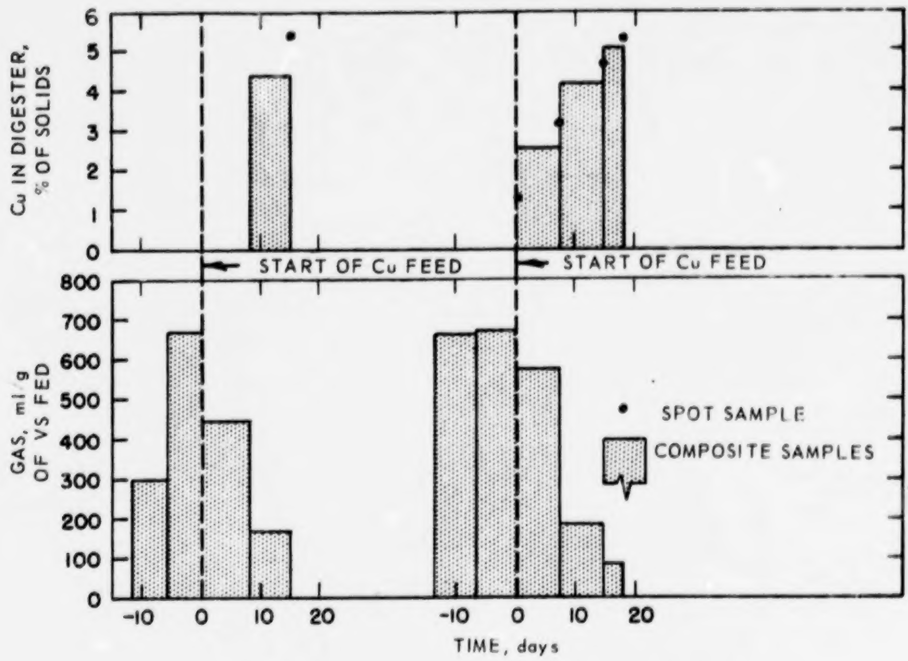

Figure 26. Performance of digester fed combined sludges from unit receiving 25 mg/liter copper, fed as copper sulfate.

Gas production from sludges obtained in parallel operation, but with no copper added, varied in weekly averages from about 600 to 900 milliliters per gram of volatile solids fed.

As previously described, all digesters were initially fed control sludges until they functioned satisfactorily; then the feeding of copper-bearing sludge was started. Gas production data for the development period are shown in the graphs. In one case a digester was operated for several weeks on sludge from sewage with 10 milligrams per liter of copper and then continued on sludge from sewage with a higher copper level. Periods of subnormal gas production were observed during the sludge development period. These were followed in some instances by abnormally high gas production periods, which resulted from accumulation of undigested material during the preceding period.

Where serious reduction of gas production occurred, the experiment was repeated and a confirming observation made. In the digestion of primary sludge from sewage containing 10 milligrams per liter of copper fed as copper cyanide complex (Figure 19), four runs were made. In the first run the digester was functioning normally, but a mechanical failure ended the run prematurely. In runs II and III a severe effect on the digester was indicated shortly following initiation of the feeding of the copper-bearing sludge. These runs were initiated on digesters with short development histories, and there was a question as to their being in normal operation when metal feeding was started. In the fourth run normal digestion continued throughout an extensive period. It appears that 10 milligrams per liter of copper is near the level at which digestion is significantly affected. The two failures suggest that copper is more likely to affect the digestion process during the initial development stages than after the digestion process is well established.

Data on the copper content of the digested sludges are shown in Figures 21 through 26. The average copper concentration in the sludge feeds is given in Table 21. Copper concentrations in sludges are proportional to the concentration of suspended matter in the sludge since copper is predominantly a part of the suspended matter in sludges. In comparisons of data from several plants, the expression of copper content on a per-unit-weight-of-suspended-matter basis is advantageous. The basis could be total suspended matter or volatile suspended matter; the former was chosen. Any ratio of copper to solids has disadvantages as a basis for relating digester performance to copper content. One disadvantage is that as interference with digestion occurs, less material is destroyed in the digester. Organic matter accumulates; and as digestion grows progressively worse, the quantity of copper per unit of suspended matter in the sludge decreases. The more critical item is that it seems logical that toxicity would be a matter of copper in solution in the water surrounding the microorganisms and, therefore, for soluble copper, the concentration basis would be most useful; however, the establishment of a relationship between effect on digestion and copper in solution is complex. The concentration of copper in solution in a sludge feed would be significantly altered in the digester by different environmental conditions, such as pH, alkalinity, and presence or production of precipitating or complexing agents. A complicating factor is that copper may be adsorbed on sludge. It was demonstrated that portions of the sorbed copper could be brought into solution by prolonged agitation. Such sorbed copper could be as important as copper in solution if it returned to solution as adsorption equilibrium was established in the digester.

Table 21. COPPER IN SLUDGES FED TO DIGESTERS

Copper in sewage, mg/liter	Form of copper fed	Primary sludge			Excess activated sludge		
		Copper		Total suspended matter mg/liter	Copper		Total suspended matter, mg/liter
		mg/liter	% of total suspended matter		mg/liter	% of total suspended matter	
5	CuCN Complex	73	0.32	23,000	89	1.8	5,000
10	CuCN Complex	140	0.76	19,000	–	–	–
10	$CuSO_4$	280	0.89	32,000	160	6.5	2,500
15	$CuSO_4$	230	0.83	28,000	210	6.2	3,400
25	$CuSO_4$	490	2.1	23,000	430	13.1	3,300

Discussion

This research was intended primarily to relate copper concentration in raw sewage to sludge digestion difficulties. It appears judicious to limit comment on soluble copper in digesters to stating that the maximum concentration of copper in solution (reactive soluble copper) in infrequent grab samples of digesters with normal gas production was 0.7 milligram per liter. This contrasts sharply with the concentration values of several hundred milligrams per liter of total copper in many samples. The subject of soluble copper in digesters will be more extensively considered in later studies.

Data on the relation of copper in sludges and digestion or treatment difficulties may be a useful by-product of the work. A sludge sample, particularly digested sludge, represents a composite accumulated over a long period of time. Thus, measurement of copper in the sludge may provide a means of estimating the average concentration of copper in sewage received over an extensive period. Subsequently, a judgment of limited certainty on whether or not copper is responsible for treatment difficulties can be made on the basis of sludge analysis.

Studies of the effect of slug doses of copper on sludge digestion were made in association with the studies of the effect of slug loads on the activated-sludge process (13). Slug doses of 4 hours in duration and ranging up to 410 milligrams per liter of copper were fed to the activated-sludge plant. Primary sludge and activated sludge were collected at the approximate times of maximum concentration of copper, as the slug progressed through the process. These sludges were promptly fed to sludge digesters, which were operating normally on control sludge. In no case was the gas production reduced following feeding of these copper-bearing sludges.

Experiments on the effect of slug doses were limited to the one form of copper, $CuSO_4$, because the hazard involved with slugs of cyanide would make their occurrence in practice rare.

Summary

Copper continuously present in concentrations ranging from 0.4 to 25 milligrams per liter in the raw sewage entering a complete pilot activated-sludge treatment plant reduced BOD removal efficiency zero to 7 percent, roughly in proportion to metal concentration, after the plant became acclimated to the metal. Two forms of copper, copper sulphate and copper cyanide complex, had about the same effects after the system had become acclimated. The process was 50 to 79 percent efficient in removal of copper. From about 25 to 75 percent of the copper in the final effluent was in solution.

Four-hour slug doses of copper as copper sulphate in concentrations greater than 50 milligrams per liter had severe effects on the efficiency of an unacclimated system. The system returned to normal in about 100 hours. Slugs of copper cyanide complex had much more severe maximum effects, but the system returned to normal in about 24 hours. Copper in slug doses of copper sulphate is largely adsorbed by the activated sludge and slowly released, whereas copper cyanide slugs pass through the system in normal detention times.

The maximum concentration of copper that does not have a detectable effect on treatment efficiency is concluded to be 1 milligram per liter. Slug doses of a few hours duration with up to 50 milligrams per liter copper as copper sulphate or 10 milligrams per liter copper as copper cyanide complex have but a slight effect on treatment efficiency.

The digestion of sludges obtained from sewage to which copper in known concentrations was fed continuously was observed. Digester performance, as measured by gas production, is indicated in Table 22.

Table 22. GAS PRODUCTION OF DIGESTERS FED COPPER

Copper in sewage, mg/liter	Primary sludge	Combined primary and excess activated sludge
5	Normal	Normal
10	Normal	Subnormal
15	Subnormal	Subnormal
25	Subnormal	Subnormal

Slug doses of copper in the sewage did not affect digestion of the resultant sludges when the sludges were fed as a single feed to a normally operating digester. The maximum slug dose tested was 410 milligrams per liter of copper fed as copper sulfate.

CHAPTER III. ZINC*

The efficiency of treatment of sewage containing zinc was studied by operation of pilot activated-sludge plants. Sewage from a common source was fed to three replicate plants. Zinc solutions were introduced continuously to the feed of two of the plants to produce selected constant concentrations; one plant was operated with no metal addition to the feed. Differences in effluent quality, as measured by BOD, COD, suspended solids, and turbidity, between the zinc feed units and the unit receiving the unaltered sewage were attributed to the presence of zinc in the feed.

The digestion of the zinc-bearing sludges was studied by operation of bench-scale digesters on sludge feeds obtained from the activated-sludge plants. Differences in gas production between the digesters receiving control sludge and those receiving the zinc-bearing sludges were attributed to the zinc in the sludge.

The objectives of the research were to determine the level of zinc that can be tolerated in waste waters without reducing the efficiency of biological processes in removing the organic matter or in stabilizing the sludges, and to determine the efficiency of the process in removing zinc.

PLANT DESCRIPTION AND OPERATION

The pilot activated-sludge plants were designed to simulate standard activated-sludge plants of the spiral-flow type The activated-sludge plant included: primary settling, aeration with continuous sludge return, and secondary settling. Thus opportunity existed for precipitation, reduction, and complexing such as might occur during primary settling in an actual situation before a biological process is reached. Effects were related to metals added to the incoming sewage rather than to metals added to some specific plant component. The units are illustrated in Figure 2. Capacity and loading factors for the plant are given in Table 23. Sewage was fed to the units at a constant rate. Sludge from the final settler was pumped continuously to the head of the aerator at a rate of about 35 percent of the sewage feed flow. An automatic device, activated once per minute, diverted the return sludge about 5 percent of each minute to a collecting vessel.

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*Material in the chapter published previously in *Proceedings of 17th Industrial Waste Conference.* Purdue University. See Reference 16.

Table 23. PILOT-PLANT DESIGN DATA AND LOADING FACTORS

Unit	Loading Factor	
Primary settler	Capacity	4.6 gal
	Detention time	1.2 hr
	Surface overflow rate	142 gpd/ft^2
Aeration tank	Capacity	23.6 gal
	BOD loading	69 lb/day/1,000 ft^3 aeration tank volume
		0.87 lb/day/lb VS under areation
	Aeration period	6 hr
Final settler	Capacity	7.9 gal
	Detention time	2 hr
	Surface overflow rate	102 gpd/ft^2

This procedure wasted about 25 percent of the suspended matter in the aeration tank each day.

The sewage available in the area where the pilot plant was located, while of essentially domestic origin, had an average BOD of about 75 milligrams per liter because of high ground-water infiltration. Fortification of this sewage with dog food produced a sewage showing characteristic behavior and adequate strength. Dry granular dog food was ground, soaked in water overnight, homogenized in a large blender, and added to the sewage at a rate of 1.2 grams(air dry) per gallon.

The sludge digesters were 5-gallon glass carboys, fitted with pumps for mixing the digester contents. The digesters were maintained at 30°C in a constant temperature room. Gas was collected in a floating-cover gas holder, and the volume was measured daily at atmospheric pressure and at 30°C. Digesters were operated on primary sludge feeds alone and on combined primary plus excess activated sludge. Sludge from the primary settler was withdrawn once per day. Excess activated sludge was withdrawn from the secondary settlers once each day and fed to the digester without delay. A volume of mixed digester contents equal to the sludge fed was removed once each day from the digesters prior to feeding. About 35 percent of the volatile matter in combined sludge feeds was from excess activated sludge and 65 percent, from primary. This is approximately the same relationship of primary and excess activated sludge as was produced in the pilot plants. Digester loading information is summarized in Table 24.

Table 24. LOADING FACTORS FOR DIGESTERS

Item	Primary sludge digester	Primary and excess activated-sludge digester
Capacity, liters	8	16
Detention, days	17	16
Loading, lb VS/day/1,000 ft ^{3} of digester volume	88	40

ZINC SOURCES AND FORM IN LIQUID WASTES

A principal source of liquid wastes containing zinc is the metal plating industry; two types of electroplating baths are used, acid baths and alkaline cyanide baths. Acid zinc baths are used most extensively in galvanizing steel wire and strip. Almost all acid zinc-plating processes employ sulfate, chloride, or mixed chloride-sulfate baths. The alkaline cyanide solution used in the major alkaline processes is a mixture of sodium zincate and zinc cyanide complexes, with an excess of sodium cyanide and hydroxide. A zinc-mercury process is also employed. The plating solution is similar to the conventional alkaline cyanide bath with the addition of a mercury salt equal to a ratio of mercury to zinc of about 1 to 100.

Zinc is also present in wastes from the manufacture of organic materials such as acrylic fiber, rayon, cellophane, and special synthetic rubbers. The historical cases of water pollution by zinc involved wastes from mining and ore processing. Corrosion of galvanized iron pipe used in household and factory distribution systems may contribute a significant amount of zinc to waste waters.

In this investigation zinc was fed to the sewage in two forms, as zinc sulfate and in the form found in a typical alkaline cyanide plating bath (9). The plating bath formulation was as follows:

Item	Grams per liter
Zinc cyanide, $Zn(CN)_2$	60
Sodium cyanide, $NaCN$	23
Sodium hydroxide, $NaOH$	53

The zinc is present in this bath in the following forms:

$$Na_2Zn(CN)_4 \rightleftharpoons 2Na^+ + Zn(CN)_4^{=}$$
$$Zn(CN)_4^{=} \rightleftharpoons Zn^{++} + 4(CN)^-$$
$$Na_2Zn(CN)_4 + 4NaOH \rightleftharpoons Na_2ZnO_2 + 4NaCN + 2H_2O$$
$$Na_2ZnO_2 \rightleftharpoons 2Na^+ + ZnO_2^{=}$$
$$ZnO_2^{=} + 2H_2O \rightleftharpoons Zn^{++} + 4(OH)^-$$

Experimentation with zinc in concentrations greater than a few milligrams per liter in the form involving cyanide and cyanide complexes has limited practical significance because of limitations usually imposed on permissible concentrations of cyanides in sewage on the basis of health hazards.

When zinc and cyanide combinations are used in experiments, the possibility of effects from the cyanide ion itself must be considered. Previous investigations have shown that cyanide in sewage is biologically destroyed in acclimated aerobic biological systems; and once a system is acclimated, the cyanide has no significant effect on treatment efficiency(12). The effects of cyanide on anaerobic processes has also been investigated. A cyanide concentration of 16 milligrams per liter in the sludge feed was reported to have no effect if the digester is first acclimated by low initial doses (14).

SAMPLE COLLECTION AND ANALYSIS

Samples for routine removal-efficiency measurements of BOD, COD, and suspended matter were collected by automatic mechanical samplers, which diverted the stream to be sampled to a refrigerated compositing carboy for 15 seconds at 15-minute intervals. The samples were composited over 24-hour periods. For measurements of the state of zinc (in solution or suspension), grab samples were collected. The filtrates containing the zinc in solution were composited for weekly periods. An extensive sampling program was used to balance the zinc fed the unit with the zinc in the effluents plus accumulation of zinc in the aerator. The balances were usually made for 1-week periods. Samples of each withdrawal of primary and excess activated sludge were composited over the balance period.

Grab samples of final effluent were collected once per day for turbidity analyses. These samples were settled for an additional 30 minutes in beakers, and turbidity measurements were made on the decanted supernatant. Thus the efficiency of the final settlers was not involved in the measurement. The turbidity reported is that from material not removable by practical sedimentation methods.

Each digester feed and digested sludge withdrawn was sampled each day. These daily samples were composited for weekly periods and analyzed for zinc and for total suspended and volatile suspended matter. Gas production per gram of volatile solids fed was computed on a weekly basis with gas produced for a weekly period lagging by 1 day the feed compositing period. Grab samples of digested sludge were also collected for metal analyses.

All analytical procedures with the exception of zinc were essentially those outlined in *Standard Methods*, 10th and 11th Editions (1,10). In the BOD test the dissolved oxygen measurements were made by the Alsterberg azide modification of the Winkler method. Desired concentrations of the samples were prepared by the cylinder dilution technique. All BOD data reported are for samples incubated 5 days at 20°C. The COD determinations of plant feed and primary effluent were assayed using 0.25 N dichromate; final effluents were assayed using 0.025 N dichromate. Following 1 hour of refluxing, silver sulfate was added. The COD's were all corrected for chloride oxidation.

The zinc content of the various samples was determined with a recording polarograph. A dropping mercury electrode, with a 3-second drop time, in conjunction with a saturated calomel electrode was used to record the current voltage curve. The samples for polarographic assay were wet-ashed with a nitric-sulfuric acid mixture; resistant samples were treated with perchloric acid. The samples were taken to cessation of fumes on an electric hot plate. The polarographic assay consisted essentially of dissolving the acid-digested sample in 1-M NH_4Cl-NH_4OH electrolyte, filtering, and recording the current voltage curve between -1.2 and -1.6 volts. The height of the diffusion curve at -1.4 volts was used as the measurement of zinc. Triton X-100 was used as maximum suppressor. Addition of zinc to various samples gave satisfactory recovery. The background zinc content of the sewage used in this study was approximately 0.1 milligram per liter. To determine soluble zinc, the samples were passed through an HA45 Millipore membrane.

Samples for cyanide determinations were first treated to separate interfering substances; then each sample was refluxed for two 1-hour periods. The sum of the cyanide determined in each of the two 1-hour periods was reported as total cyanide. Good recoveries in the first hour were demonstrated.

ZINC AND ACTIVATED-SLUDGE TREATMENT

Continuous Feeding

An experimental run of the activated-sludge plant was made at each of three levels of zinc in the sewage feed, 2.5 10, and 20 milligrams per liter. The zinc was fed in the form of zinc sulfate in each concentration; in addition, zinc in the form of the alkaline cyanide plating bath formula, referred to as complexed zinc, was fed at the 10-milligram-per-liter zinc level. These three runs were made with continuous addition of zinc to the sewage. For each zinc level, 2 weeks or more was allowed to pass between the initiation of feeding the metal to a normal sludge and the collection of the first samples for use in obtaining data on effluent quality for an acclimated system. Fifteen to thirty-four 24-hour composite samples of the feeds, primary effluents, and final effluents were analyzed. The average BOD, COD, suspended matter, and turbidity values for the final effluent of the

Table 25. QUALITY OF FINAL EFFLUENTS FROM CONTROL AND ZINC-FED UNITS

Zinc in sewage, mg/liter	Form of zinc added	Avg BOD, mg/liter	Avg COD, mg/liter	Avg suspended matter, mg/liter	Avg turbidity, stu
0	Control	13	39	7	18
2.5	$ZnSO_4$	15	40	8	22
0	Control	13	44	10	16
10	$ZnSO_4$	18	49	17	17
10	Complexed zinc	22	57	16	27
0	Control	11	58	7	18
20	$ZnSO_4$	15	68	16	46

control and zinc fed units are presented in Table 25. Differences in sewage feed characteristics among the plants were predominantly no greater than differences attributable to sampling and analytical variations. Characteristics of the sewage feed are given in Table 26. The sewage feed was generally near or slightly below pH 7.0, and the final effluent near 7.5.

Table 26. CHARACTERISTICS OF SEWAGE FEEDS AND PRIMARY EFFLUENTS

Zinc concentration, mg/liter	Zinc form	BOD		COD		Suspended matter	
		Primary feed, mg/liter	Primary effluent, mg/liter	Primary feed, mg/liter	Primary effluent, mg/liter	Primary feed, mg/liter	Primary effluent, mg/liter
0	Control	289	184	483	306	299	157
2.5	$ZnSO_4$	313	195	492	315	326	169
0	Control	228	162	469	323	240	148
10	$ZnSO_4$	271	182	555	342	394	195
10	Complexed zinc	245	179	552	376	331	208
0	Control	262	199	512	390	265	179
20	ZnSO	268	236	517	426	274	179

Analytical data for the run with a zinc concentration of 2.5 milligrams per liter are presented as cumulative percent frequency plots on logarithmic probability paper in Figure 27. This presentation

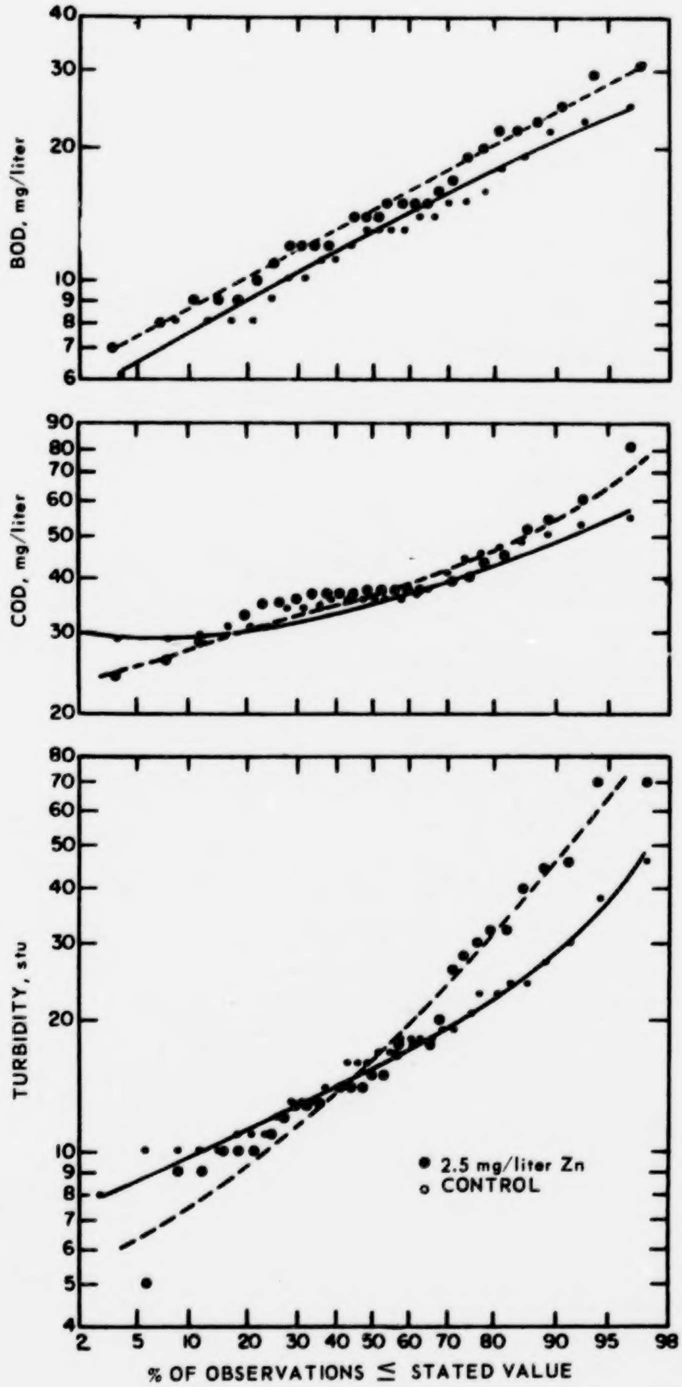

Figure 27. Cumulative frequency data on quality of final effluents with zinc concentration of 2.5 mg/liter fed as zinc sulfate.

of the complete data makes comparisons of variations convenient. From Table 25 and Figure 27 a slightly lower quality of effluent in the unit fed zinc may be inferred. Statistical analysis of the variations in the data indicates a strong likelihood that these differences could have occurred by chance alone in randomly selecting 30 some values from an infinite number of measurements; therefore, from both statistical inference and practical considerations, the indicated differences are considered insignificant.

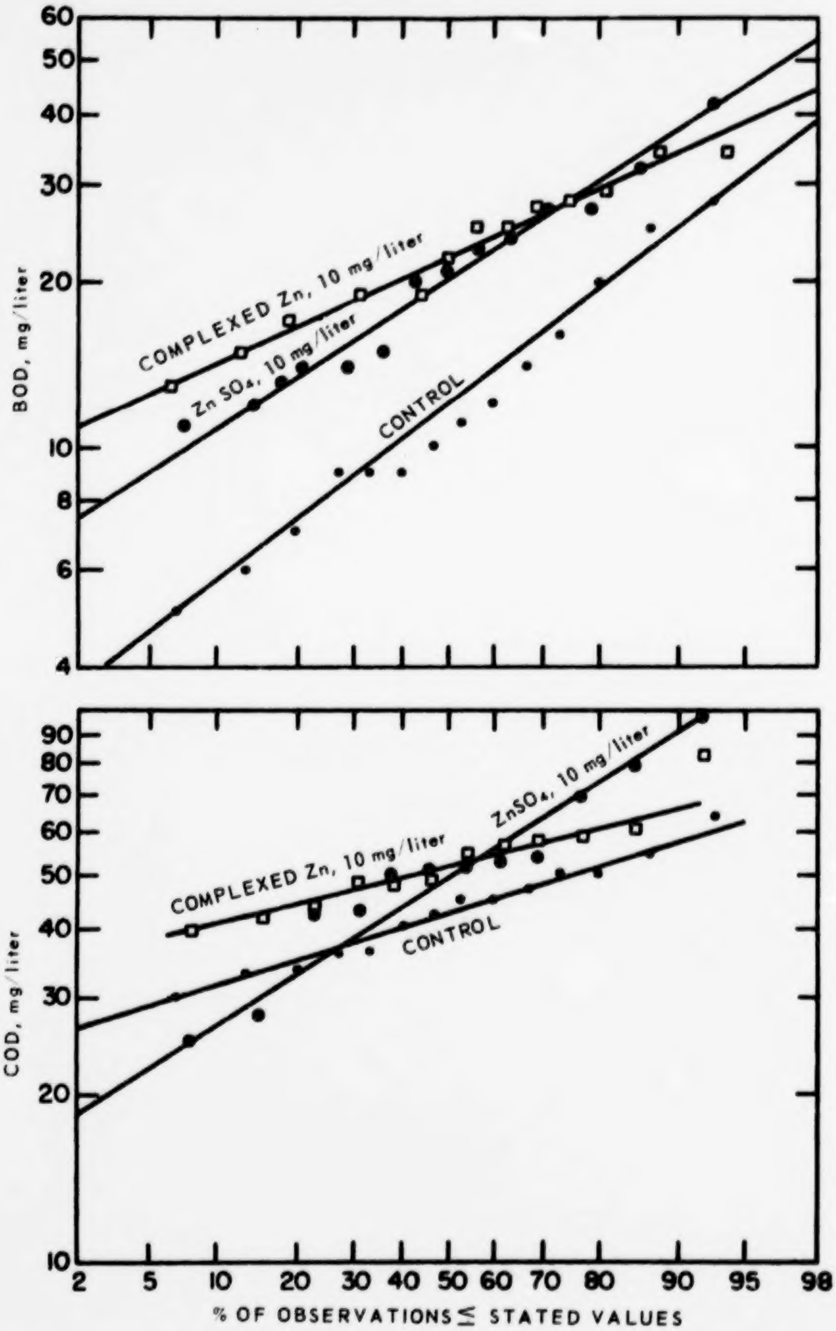

Figure 28. Cumulative frequency data on quality of final effluents with zinc concentration of 10 mg/liter in sewage feed.

Some of the runs with zinc concentrations of 10 milligrams per liter fed as zinc sulfate and the same concentration fed as the alkaline cyanide bath were made simultaneously in parallel. These data are shown as cumulative frequency plots in Figure 28. The differences between the data for the two forms of zinc were not significant. The differences between the data with either form of zinc and the control are significant, statistically speaking. They have a low likelihood of having occurred by chance alone.

Correlation coefficients were computed for aerator loading, aerator suspended-matter level, temperature, COD, and BOD values of final effluents for each of the runs. The correlations were not significant, since no substantial relation between the variables was indicated. The differences that occurred in aerator solids level and loadings among the units did not, therefore, appreciably affect results.

The ultimate fate of zinc in the treatment process during the runs with zinc sulfate concentrations of 2.5 and 10 milligrams per liter is shown in Table 27. A minor part of the zinc was removed in primary settling; a large part became associated with the aerator liquor suspended matter. These figures are the mean values of the weekly material balances in zinc described previously. The imbalance data refer to the average degree of success in the balances between zinc fed and zinc accounted for. Zinc in the sewage supply was not included in the balance because measurements indicate a level of about 0.1 milligram per liter, which, at the most, is 4 percent of the zinc fed. This background zinc may in part account for the positive imbalance at the 2.5-milligram-per-liter level.

Table 27. ZINC DISPOSITION IN PROCESS OUTLETS

Zinc in sewage, mg/liter	Form of zinc fed	Primary sludge	Excess activated sludge	Final effluent	Imbalance
		Zinc, mg/liter			
2.5	$ZnSO_4$	64	120	0.12	–
10	$ZnSO_4$	375	328	0.88	–
		Zinc fed in outlet, %			
2.5	$ZnSO_4$	13	85	5	+12
10	$ZnSO_4$	14	63	9	-14

The average efficiencies of the processes in removing zinc, based on zinc determinations in effluents, are given in Table 28. The complexed zinc was as easily removed by an acclimated system

Table 28. EFFICIENCY OF PROCESS IN ZINC REMOVAL

Zinc in sewage, mg/liter	Form of zinc fed	Removed by primary treatment, %	Removed by complete activated-sludge treatment, %
2.5	$ZnSO_4$	13	95
10	$ZnSO_4$	14	89
10	Complexed zinc	–	96
16	Complexed zinc	8	–
20	$ZnSO_4$	–	74

as was the zinc sulfate form. A distinct difference in the effect of the two forms was demonstrated in the acclimation period. In the experiments with continuous feeding of complexed zinc at a concentration of 10 milligrams per liter and zinc sulfate at 20 milligrams per liter, data on effluent quality were obtained during the first few days following introduction of zinc to the unit feeds. The sludges were developed on feeds to which no zinc had been added. The acclimation phenomena of these sludges is demonstrated by the turbidity data shown in Figure 29. The first sample of the feed containing complexed zinc, collected about 30 hours after initiation of the metal feed, had a turbidity of almost 80 standard units. The turbidity declined in subsequent samples and, after about 5 days, reached a level that prevailed during the remainder of the run. This improvement in turbidity paralleled the decrease in cyanide in the final effluent. In the first samples cyanide in the final effluent was practically

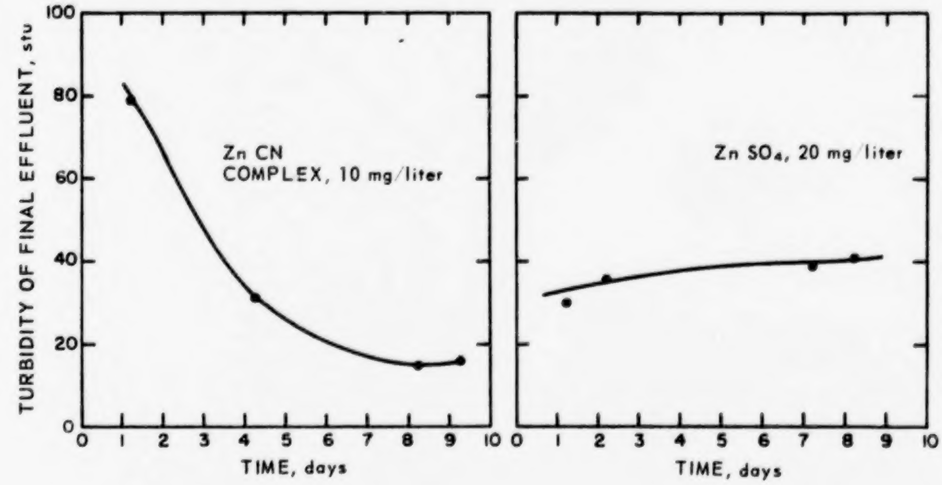

Figure 29. Comparison of acclimation to complexed zinc and zinc sulphate.

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equal to that fed. In subsequent samples the cyanide level was progressively lower until samples collected on the fifth and succeeding days had at the most only traces of cyanide. Acclimation to the alkaline cyanide bath is apparently a phenomena of adaption of the system to degradation of the cyanide. Feeding of zinc sulfate, on the other hand, resulted in a turbidity in the first sample of final effluent collected of about the same level as that prevailing during the run. Thus, acclimation of this system to zinc occurred in a few hours.

The state of the zinc, whether in solution or in insoluble form, was of interest. Zinc not in solution would not be expected to exert a toxic action. Data on zinc in solution in the primary and final effluents are presented in Table 29. The values given are average; the range about these averages was great.

Table 29. ZINC CONCENTRATION AND FORM IN PROCESS

Zinc in sewage, mg/liter	Form of zinc fed	Primary effluent, mg/liter		Final effluent, mg/liter	
		In solution	Total	In solution	Total
2.5	$ZnSO_4$	0.05	2.05	0.02	0.12
10	$ZnSO_4$	0.64	8.9	0.18	0.88
10	Complexed zinc	0.94	9.8	0.09	0.39
20	$ZnSO_4$	10.4	19.8	4.29	5.16

Slug Doses*

The reaction of the activated-sludge process to a 160-milligram-per-liter slug dose of zinc was studied. The system was acclimated to 5 milligrams per liter of zinc for 1 month prior to the slug. The slug consisted of zinc in the form of zinc sulfate, and lasted for 4 hours in the influent sewage. After the slug, the 5-milligram-per-liter zinc dose was continued. Eight hours after the slug, the solids in the final settler showed slight bulking, but after 24 hours the settling characteristics of the sludge were satisfactory. Microscopic examination of the mixed liquor before, during, and several days after the slug showed that the higher forms were not affected by this concentration of zinc.

The response of the system is shown on Figure 30. There was a serious upset of the plant for about 30 hours after the start of the slug but the plant was producing effluent of pre-slug quality 40 hours after the start of the slug.

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*The material in this section was completed after original publication of Reference 16.

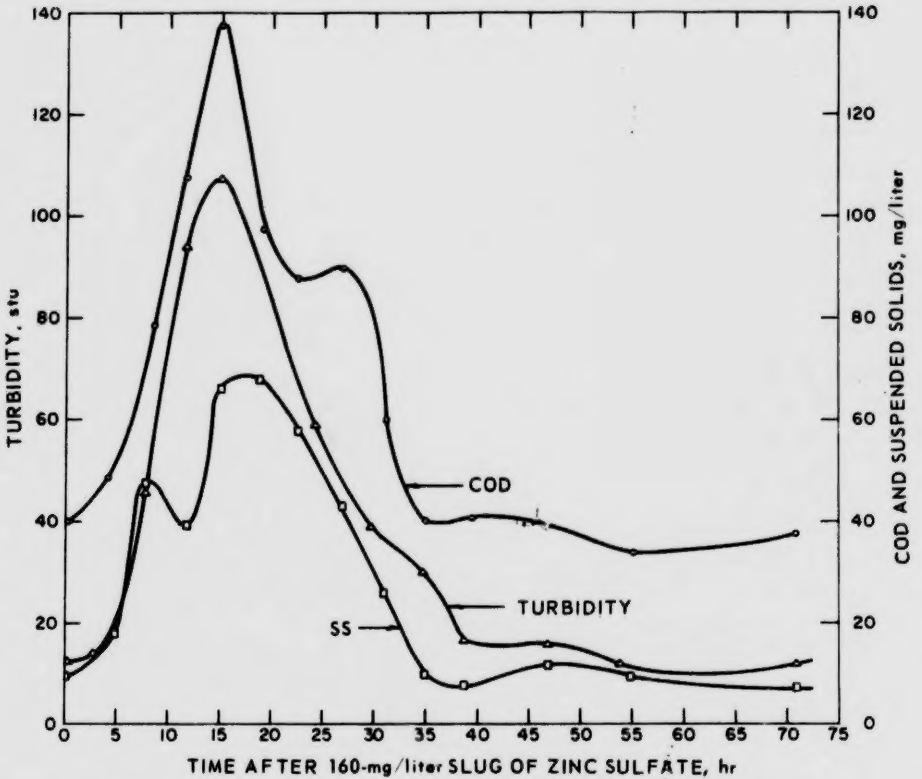

Figure 30. COD, turbidity, and suspended solids of final effluent.

The primary and waste activated sludges removed from the plant in a 3-day period after the slug accounted for 67 percent of the zinc added; approximately 33 percent of the zinc from the slug went out with the final effluent. A material balance for zinc in the slug accounted for 104 percent of the metal. The zinc discharged in the final effluent was predominantly in an insoluble form and did not exceed 9 milligrams per liter at any time, as shown on Figure 31.

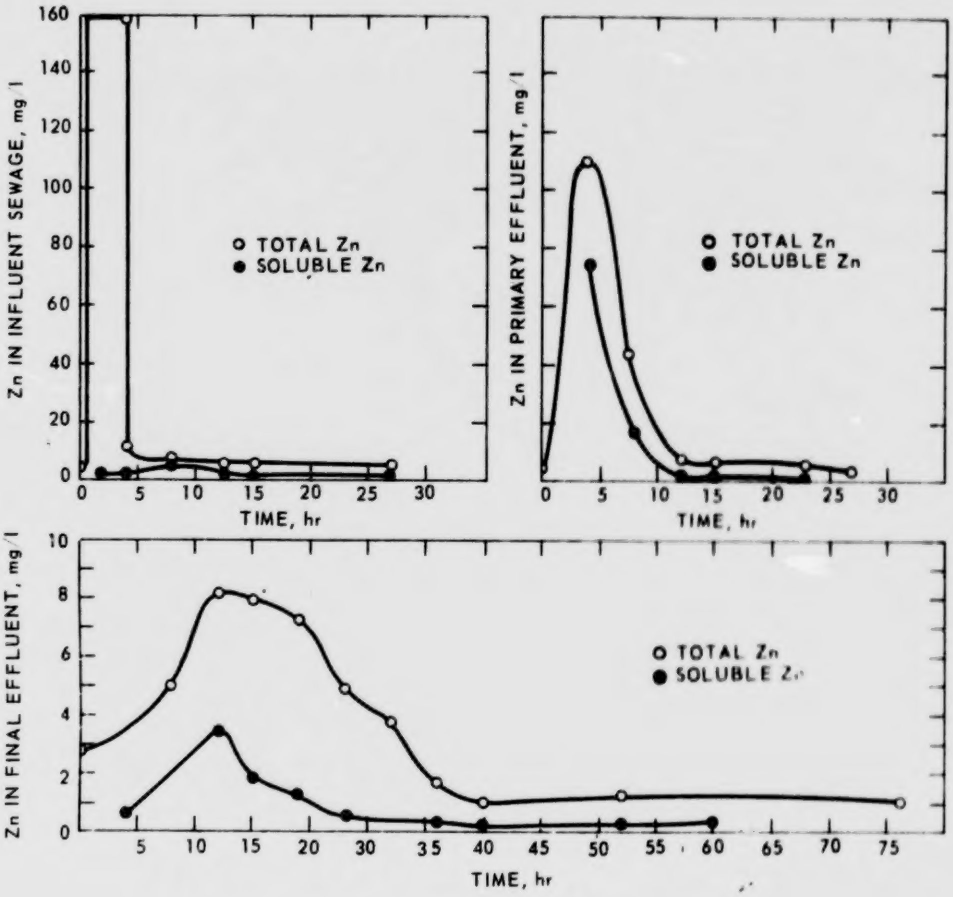

Figure 31. Zinc in sewage and effluents, slug of 160 mg/liter for 4 hours.

This figure also shows an unexpected behavior of the zinc during the slug study; the soluble zinc content of the influent sewage was quite low in contrast to the soluble zinc content of the primary effluent. This can probably be explained by dilution of the slug in the primary settler causing re-solution of insoluble zinc in the influent sewage, and complexing reactions occurring during the detention period.

ZINC AND SLUDGE DIGESTION

The average gas production from digestion of zinc-bearing sludges for 7-day periods, the interval of daily feed compositing, is shown in Figures 32 through 35. The digesters were seeded originally with sludge from a municipal sewage treatment plant. Sludges from the activated-sludge plant that received no addition of zinc to its feed were fed for a week or more before the feeding of zinc-bearing sludge was started. Production of gas during this normalization period is shown on the graphs. Gas produced by sludges from the control unit ranged from approximately 600 to 900 milliliters per gram of volatile solids fed.

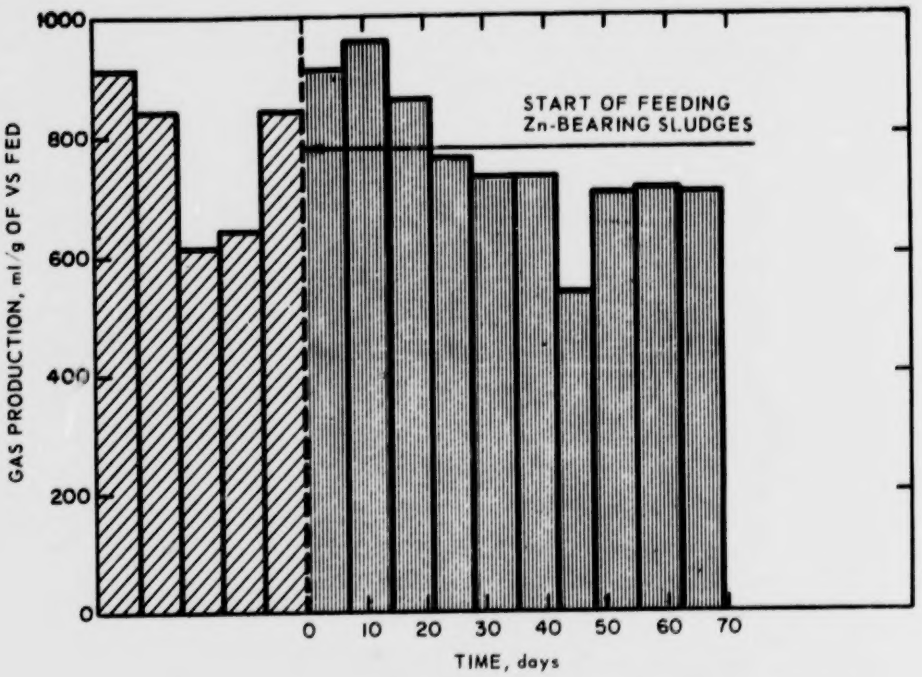

Figure 32. Gas production of combined sludges from sewage fed 10 mg/liter zinc as zinc sulfate.

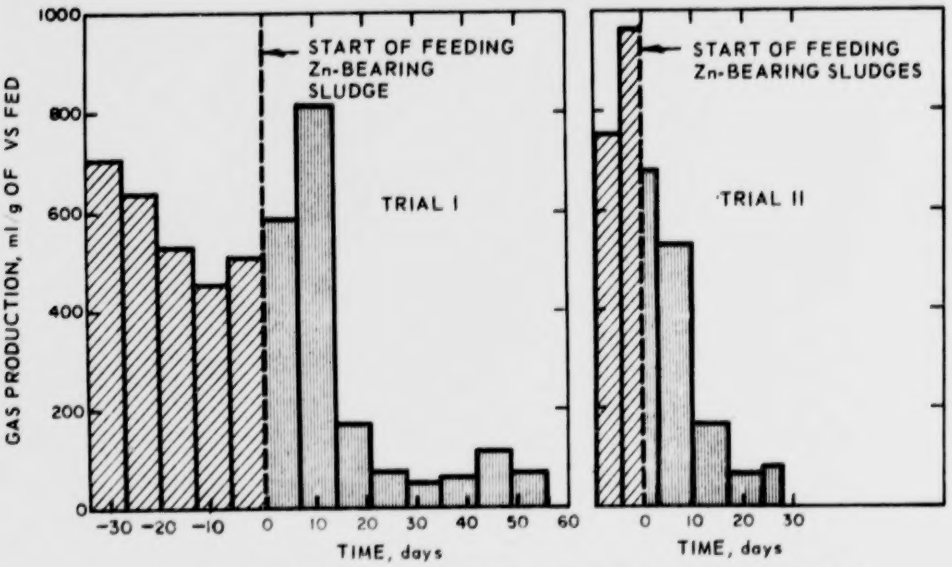

Figure 33. Gas production of combined sludges from sewage fed 20 mg/liter zinc as zinc sulfate.

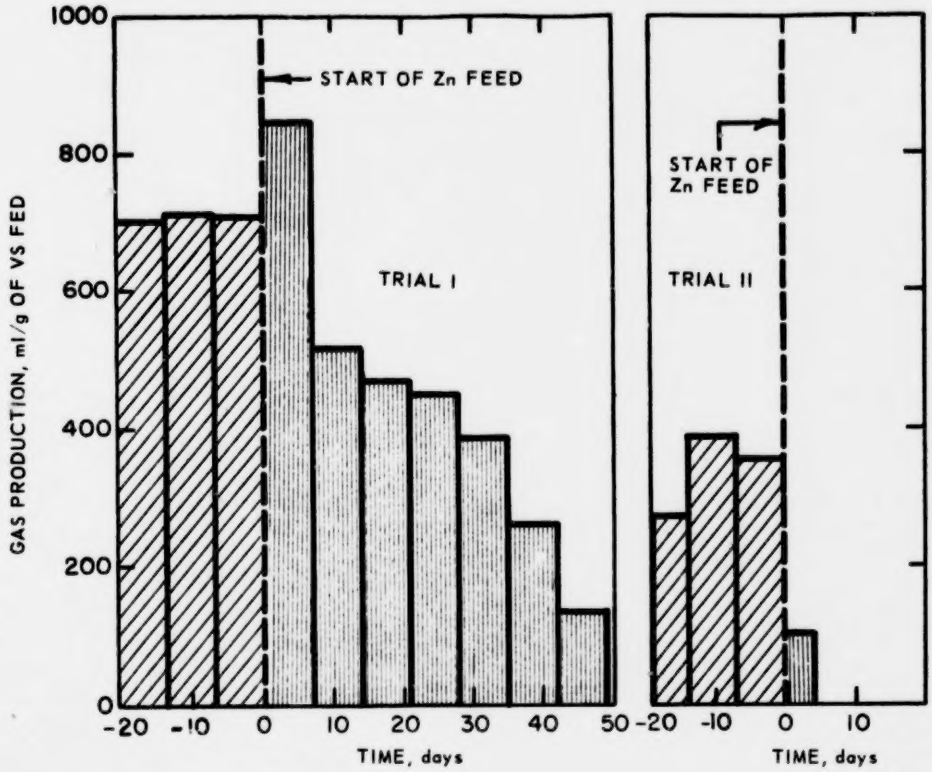

Figure 34. Gas production of primary sludge from sewage fed 16 mg/liter zinc as complexed zinc.

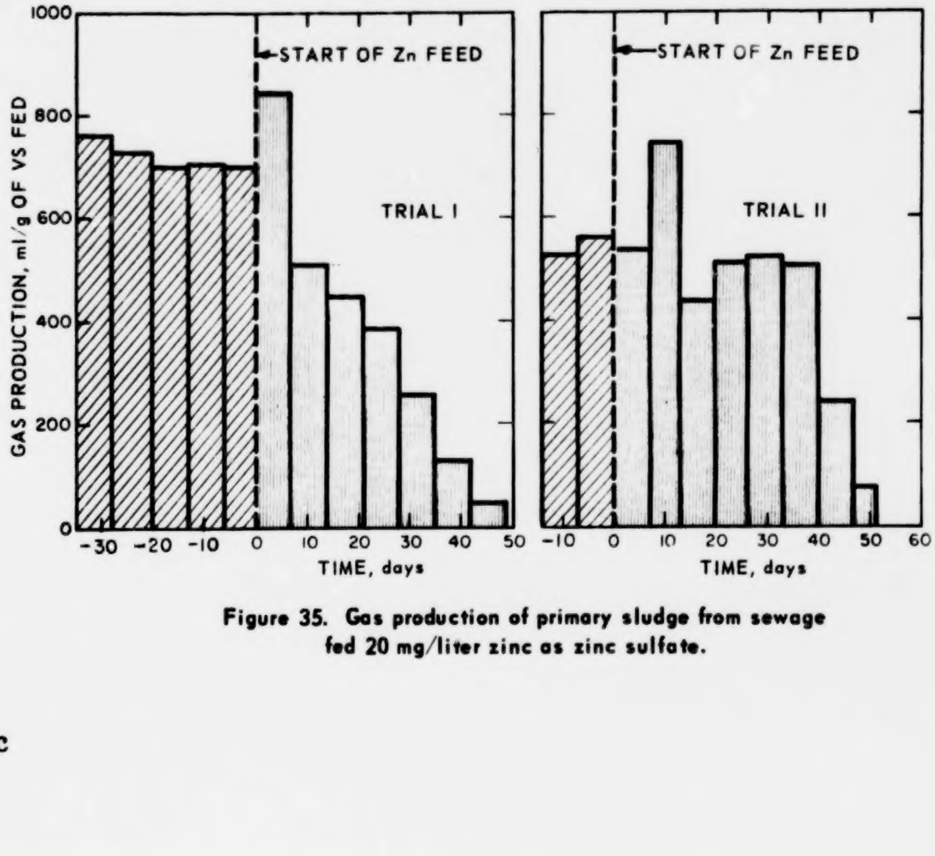

Figure 35. Gas production of primary sludge from sewage fed 20 mg/liter zinc as zinc sulfate.

Where a serious reduction in gas production occurred, the experiment was repeated and a confirming observation made. The experiments with effects of zinc on digesters were essentially limited to a zinc sulfate feed because high cyanide levels are prohibited, as discussed previously. One exception was a run made with digestion of primary sludge from sewage fed complexed zinc in a concentration of 16 milligrams per liter. This concentration of zinc in the form of the alkaline cyanide bath corresponds to a concentration of CN^- of 18.3 milligrams per liter. This experiment showed that sludge from sewage with a zinc level of 16 milligrams per liter together with a CN^- level of 18.3 milligrams per liter would not digest at normal rates when introduced to an unacclimated normally functioning digester. In the second experiment at this concentration the feeding of zinc-bearing sludge was inadvertently initiated before the digester was producing normal volumes of gas. The gas production rate was affected much more rapidly in this case.

Data on the concentration of zinc in the primary sludges, excess activated sludges, and digested sludges for three levels of zinc in the sewage are given in Table 30. Zinc concentrations in sludges are proportional to the concentration of suspended matter in the sludge since the zinc is predominantly a part of the suspended matter. In order to compare zinc data among sludges with varying solids concentrations, the zinc is expressed as a percent of the total and volatile residues in the sludges.

Table 30. TOTAL ZINC IN SLUDGES

Zinc in sewage, mg/liter	Form of zinc fed	Primary sludge,			Excess activated sludge,			Digested primary sludge,			Digested combined sludges,		
		mg/liter	% of total residue	% of volatile residue	mg/liter	% of total residue	% of volatile residue	mg/liter	% of total residue	% of volatile residue	mg/liter	% of total residue	% of volatile residue
2.5	$ZnSO_4$	64	0.22	0.27	119	2.5	3.7	–	–	–	–	–	–
10	$ZnSO_4$	375	0.95	1.6	328	6.0	12	–	–	–	341	3.16	8.0
16	Complexed zinc	548	2.0	3.0	–	–	–	545	[a]	[a]	–	–	–

[a] Digestion subnormal, values change as undigested material accumulates.

Sludge in the digesters was completely mixed at times of its removal; therefore, the accumulation of zinc in the digester would follow the principle of displacement of one material, A, from a homogeneously mixed system by continuous addition of a second material, B. Theoretically, after a number of feedings equal to the digester volume divided by the daily feed volume (one detention period), the sludge of the new origin (zinc-bearing) would constitute just over 60 percent of the sludge in the digester. After four periods only a negligible percent of the original sludge would be left. In order to reach the maximum zinc concentration in the digesters, they were operated for over 60 days before terminating an experiment, if a digester continued with normal gas production. The concentration of zinc reported for digested combined sludges at the zinc level of 10 milligrams per liter is an average value after the zinc concentration in the digester had leveled off.

Data on the relation of zinc in sludges to digestion or treatment difficulties may also be a useful by-product of the work. A sludge sample, particularly digested sludge, represents a composite accumulated for long periods of time. Thus measurement of zinc in the sludge may provide a means of estimating the average concentration of zinc in sewage received over an extensive preceding period. Subsequently, a limited judgment as to whether or not zinc is responsible for subnormal treatment can be made from a few sludge analyses.

It seems logical that toxicity of the liquid surrounding microorganisms would result from zinc in solution. For this reason, in two of the runs, measurements were periodically made of zinc in solution in the sludge feeds and the digester. The data obtained are given in Table 31. The quantity of zinc in solution did not appear to follow any pattern of increase corresponding to decreases in gas production.

Table 31. ZINC IN SOLUTION IN SLUDGES

Zinc in sewage, mg/liter	Form of zinc fed	Zinc in solution		
		Sludge	Avg, mg/liter	Range, mg/liter
10	$ZnSO_4$	Primary sludge	0.31	0–1.18
		Excess activated sludge	0.06	0–0.21
		Digested combined primary and excess activated	0.17	0–0.67
16	Complexed zinc	Primary sludge	1.33	0–4.39
		Digested primary sludge	0.34	0–1.44

SUMMARY

Zinc fed continuously in concentrations ranging from 2.5 to 20 milligrams per liter of sewage entering a complete pilot activated-sludge treatment plant reduced the BOD removal efficiency a maximum of about 2 percent. Two forms of zinc, zinc sulfate and complexed zinc such as that which occurs in an alkaline cyanide plating bath, had about the same effects after the sludge became acclimated. The maximum level of zinc that will not produce a significant effect on treatment efficiency was indicated as being >2.5 and <10 milligrams per liter.

Primary treatment is not efficient in removing zinc; however, the microbial floc of secondary treatment adsorbs much zinc. The overall process is from 95 to 74 percent efficient in removing zinc at the feed levels of 2.5 and 20 milligrams per liter, respectively.

A 160-milligram-per-liter slug dose of zinc, lasting for 4 hours, caused a serious reduction in treatment efficiency for about 1 day. Forty hours after the slug the plant recovered and produced suitable effluent.

Sludges from sewage fed zinc, as zinc sulfate in a concentration of 10 milligrams per liter digested at normal rates. The combined sludges from sewage fed zinc, as $ZnSO_4$ in a 20-milligram-per-liter concentration, caused rapid failure of the digestion process. For normal digestion of the primary or combined sludges, the maximum level of zinc in sewage is between 10 and 20 milligrams per liter.

CHAPTER IV. NICKEL*

The efficiency of activated-sludge plants in the treatment of sewage containing nickel was studied. Sewage from a common source was fed to three replicate pilot plants. Nickel solutions were added to the sewage entering certain pilot plants to produce selected constant concentrations. No metal was added to the sewage entering one of the units. Differences in the quality of the effluents, as measured by BOD, COD, suspended solids, and turbidity, from the nickel-fed units and the unfed unit were attributed to nickel in the feed.

The anaerobic digestion of the nickel-bearing sludges was studied by operation of bench-scale digesters on sludge feeds obtained from the activated-sludge plants. Any differences in gas production in the digesters receiving control sludge and those receiving the nickel-bearing sludges were also attributed to nickel in the sludge.

The objectives of the research were (1) to determine how much nickel in waste waters can be tolerated without reducing the efficiency of biological processes in removing the organic matter or in stabilizing the sludges and (2) to determine the efficiency of the process in removing nickel.

PLANT DESCRIPTION AND OPERATION

The activated-sludge pilot plants were designed to simulate standard activated-sludge plants of the spiral flow types. The shape and dimensions of the activated-sludge units are illustrated in Figure 2. The nickel solutions were fed to the sewage before it entered the primary settler. Thus precipitation, reduction, and complexing that might occur during primary settling before a biological process is reached were included in the experimental conditions. Effects are related to metal additions to the incoming sewage rather than to metals added to some specific plant component. The sewage fed to the plants was either a weak sewage obtained from the Eastern Avenue interceptor or a more normal sewage from the Beechmont interceptor of the city of Cincinnati. The latter sewage was used only for a short time at one nickel concentration.

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*Material in this chapter published previously in *Journal Water Pollution Control Federation.* Washington 25, D.C. 20016. See Reference 17.

The sewage from the Eastern Avenue source was of low strength because of dilution by ground water infiltration. The weak sewage was supplemented with either fish meal or dog food to bring its organic content to a level found in strong domestic sewage since an adverse effect of metal on effluent strength probably would be exhibited at the high-level end of the range of domestic sewage strength. Dog food of the granular, dry type was ground to a fine powder and soaked over night in water; the resultant slurry was blended for 5 minutes and then mixed with sewage at a concentration of 1.2 grams (air dry) per gallon. Chemically, the dog food was considered to approach the organic matter composition of domestic sewage except for its low nitrogen content. To raise the nitrogen content of the strengthened sewage to near that found in strong domestic sewage, urine was added at the rate of 1.4 milliliters per liter. The nitrogen content of the fish food was relatively high, and no supplemental nitrogen was needed.

The sludge digesters were 5-gallon glass carboys, which were connected to pumps for mixing the digester contents. Single-stage digestion without continuous agitation was employed. The digesters were maintained at 30°C in a constant-temperature room. Gas was collected in a floating-cover gas holder; its volume was measured daily at atmospheric pressure and 30°C.

Sewage was fed to the units at a constant rate. Sludge was returned from the final settler continuously at a rate of about 35 percent of the sewage feed flow. An automatic device was activated once per minute to divert about 5 percent of the return sludge to a waste-excess activated-sludge-collecting carboy. Capacity and loading factors for the units of the plant are given in Table 32.

Table 32. PILOT-PLANT DESIGN DATA AND LOADING FACTORS

Unit	Loading factor	
Primary settler	Capacity	4.6 gal
	Detention time	1.2 hr
	Surface overflow rate	142 gpd/ft^2
Aeration tank	Capacity	23.6 gal
	BOD loading	41-63 lb/day/1,000 ft^3 aeration tank volume. 0.50-0.75 lb/day/lb VS under aeration
	Aeration period	6 hr
Final settler	Capacity	7.9 gal
	Detention time	2 hr
	Surface overflow rate	102 gpd/ft^2

Digesters were operated on primary sludge feeds alone and on primary combined with excess activated sludge. Primary sludge was withdrawn once per day from the primary settler. Excess activated sludge for digester feed was collected once per day from the final settler. The sludge accumulating in the waste-excess activated-sludge carboy was not used for digester feed because of the possibility that septic conditions during the collection period might cause nontypical metal reactions. To minimize changes of metal in solution, the sludges were allowed to consolidate only 30 minutes or less after collection. For this reason solids concentrations in the sludges were lower than those usually found in sewage treatment practice.

The digesters were thoroughly agitated once daily by means of a pump, which withdrew sludge from the bottom of the digester and returned it at the top. Digesters were fed once each day. The digesters receiving a combination of primary and excess activated sludge were fed 300 milliliters of primary sludge and 700 milliliters of excess activated sludge. This daily feed contained about 10 grams of volatile matter, approximately 60 percent of which was from the primary sludge. This is the approximate ratio of production of primary and excess activated sludge in the pilot plant. The digesters receiving only primary sludge were fed 470 milliliters of primary sludge, which contained about 10 grams of volatile matter. Digester capacity and loading parameters are given in Table 24.

NICKEL SOURCE AND FORM IN LIQUID WASTES

A common source of liquid wastes containing nickel is the metal plating industry. Usually, nickel used in plating baths is principally nickel sulphate with smaller quantities of nickel chloride and boric acid. A solution of nickel (II) sulfate was added to the sewage in this investigation.

SAMPLE COLLECTION

Samples for measurement of effects of nickel on treatment efficiency were collected by mechanical samplers. The sampler was activated by a timer at 15-minute intervals and diverted the stream to be sampled to a refrigerated collecting vessel for a period of about 12 seconds each time. The samples were composited over 24-hour periods. The analytical procedures were started within a few hours after the compositing period. Samples for studies of the effect of slug doses were collected in the same manner except that compositing periods were limited to as little as 4 hours to show peaks in effects. Grab samples were taken for some nickel concentration measurements. Samples of sludges and the final effluents were collected for making material balances between nickel fed the units and nickel in the effluents plus nickel accumulated in the aerator. Samples of each withdrawal of primary and excess activated sludge were collected and composited over the balance period of 1 week. Samples of the final effluent were collected by automatic samples at 15-minute intervals and composited for the week. Grab samples of the aerator contents were collected at the beginning and end of each balance period for nickel accumulation measurements.

ANALYTICAL METHODS

The procedures used were those outlined in *Standard Methods*, 11th edition (10). Details of alternatives selected and procedures utilized are described in the following discussion.

Biochemical Oxygen Demand

In the BOD test, the initial and final dissolved oxygen measurements were made by the Alsterberg azide modification of the Winkler method. Sample dilutions were prepared by the cylinder dilution techniques. All BOD data are for incubation at 20° C for 5 days.

Chemical Oxygen Demand

In the determination of COD, primary feed and primary effluent samples were oxidized by use of 0.25 N dichromate. For final effluent samples, 0.025 n dichromate was used. Silver sulfate catalyst was not used. No correction for chloride was made. Chloride concentrations in the sewage were normally about 40 milligrams per liter.

Nickel

Nickel analyses were made by two methods. In one method, samples relatively high in nickel content, such as sludges, were assayed by selectively precipitating nickel from an ammoniacal slurry of an acid-digested sample with dimethylglyoxime. The nickel dimethylglyoxime precipitate was then eluted from the filter paper with concentrated HC1; the filtrate was made ammoniacal; and nickel reprecipitated with dimethylglyoxime. The nickel complex was then redissolved in concentrated HC1, and the excess HC1 removed by evaporation on a hot plate. The residue was made ammoniacal and titrated with a standardized solution of Versenate in the presence of the purple dye Murexide.

In the other method, low concentrations of nickel, found in feed and final effluent samples, were assayed by the alpha-furildioxime colorimetric procedure (15). The only interfering ions usually encountered in sewage are Cu^{++} and Fe^{++}. The assay consisted essentially of adding dilute $K_2Cr_2O_7$ (to oxidize Fe^{++}) and sodium citrate (to complex Fe^{+++}) to an aliquot of the sample diluted to 100 milliliters, (adding 1 gram sodium thiosulfate, to complex Cu^{++}), adjusting to pH 8-9, and adding alpha-furildioxime dissolved in ethyl alcohol. The colored complex is extracted with 3x7 milliliters of $CHCl_3$ and diluted to 25 milliliters. The optical density at 435 millimicrons is proportional to the nickel concentration.

For both methods outlined above, recovery tests, in which standard nickel additions were made to samples, were satisfactory. Both methods are sensitive and specific for nickel.

Many samples were analyzed for both total nickel and nickel in solution. Sample aliquots for determining nickel in solution were filtered with an HA45 Millipore membrane. The filtrate was digested in a nitric and sulfuric acid mixture, and nickel was determined by the alpha-furildioxime colorimetric procedure. Many analyses showed that a portion of the nickel in the filtrate would not react with the reagent without prior acid digestion. All results reported for nickel in solution are for samples subjected to acid digestion.

NICKEL AND ACTIVATED-SLUDGE TREATMENT

Industrial wastes containing heavy metals may be discharged more or less continuously in, for example, drainage and rinse water wastes from metal plating operations, or wastes with high metal concentrations may be discharged over short periods from, for example, a plating bath dump or spill. Observations under conditions simulating both occurrences were made, that is, with nickel continuously present at constant concentration in the influent sewage and with nickel introduced as a slug dose.

Continuous Nickel Addition

Runs were made with 1-, 2.5-, 5-, and 10-milligram-per-liter concentrations of nickel continuously present in the sewage feed. A control plant received no metal and was operated in parallel during each run. The 5- and 10-milligram-per-liter runs were made concurrently with a common control unit. The average characteristics of the sewage feed during each of the runs are given in Table 33. The analytical data on sewage feed to the control and to the experimental units during each run generally were in agreement within a range attributable to sampling and analytical variations.

Before samples for efficiency studies were collected, the metal-fed units were allowed to acclimate for a 2-week period after initiation of the metal feed. Thirteen to twenty-six 24-hour composite samples of the experimental and control units were collected and analyzed during each run.

Table 33. AVERAGE CHARACTERISTICS OF SEWAGE FEEDS AND PRIMARY EFFLUENTS FOR CONTROL AND NICKEL-FED UNITS

Nickel (as $NiSO_4$) addition, mg/liter	BOD, mg/liter		COD, mg/liter		Suspended matter, mg/liter	
	Primary feed	Primary effluent	Primary feed	Primary effluent	Primary feed	Primary effluent
0	217	145	326	236	257	155
10	207	148	342	238	304	187
0	217	145	326	236	257	155
5	255	190	393	267	314	175
0	247	178	396	269	337	143
2.5	260	192	409	301	303	184
0	172	123	272	228	178	121
1.0	186	117	287	235	177	125

The quality of the final effluents from the nickel-fed units and the control units are presented in cumulative frequency distribution curves on logarithmic probability paper in Figures 36, 37, and 38. Such curves enable presentation of the complete data and rapid comparisons. Table 34 gives a brief summation of the results in arithmetic averages of final effluent determinations.

Table 34- AVERAGE CHARACTERISTICS OF FINAL EFFLUENTS FROM CONTROL AND NICKEL-FED UNITS

Nickel (as$NiSO_4$) addition, mg/liter	BOD, mg/liter	COD, mg/liter	Suspended matter, mg/liter	Turbidity, stu
0	9	40	8	4
10	14	54	17	28
0	9	40	8	4
5	13	51	16	15
0	13	59	5	10
2.5	26	63	9	29
0	21	48	11	25
1	23	51	8	34

The BOD's of the final effluents for the various runs are given in Figure 36. The data show that nickel concentrations of 2.5, 5, and 10 milligrams per liter significantly affected treatment efficiency. At 1 milligram per liter, however, there was no significant difference

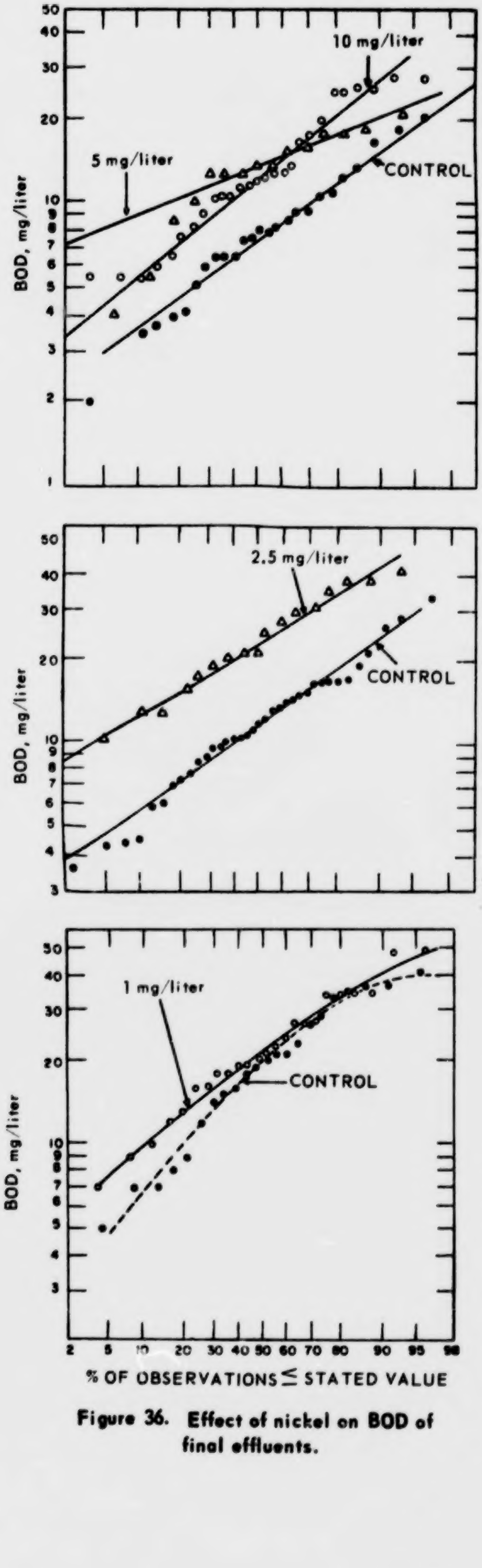

Figure 36. Effect of nickel on BOD of final effluents.

in the efficiency of the nickel-fed unit and the control unit. Data at this low nickel concentration are for sewage supplemented with fish food and for strong domestic sewage. Nickel at this level did not have a significant effect on BOD removal with either sewage. The BOD data for the 2.5-milligram-per-liter run is interesting because a greater effect was shown than would be expected from the 5- and 10-milligram-per-liter runs.

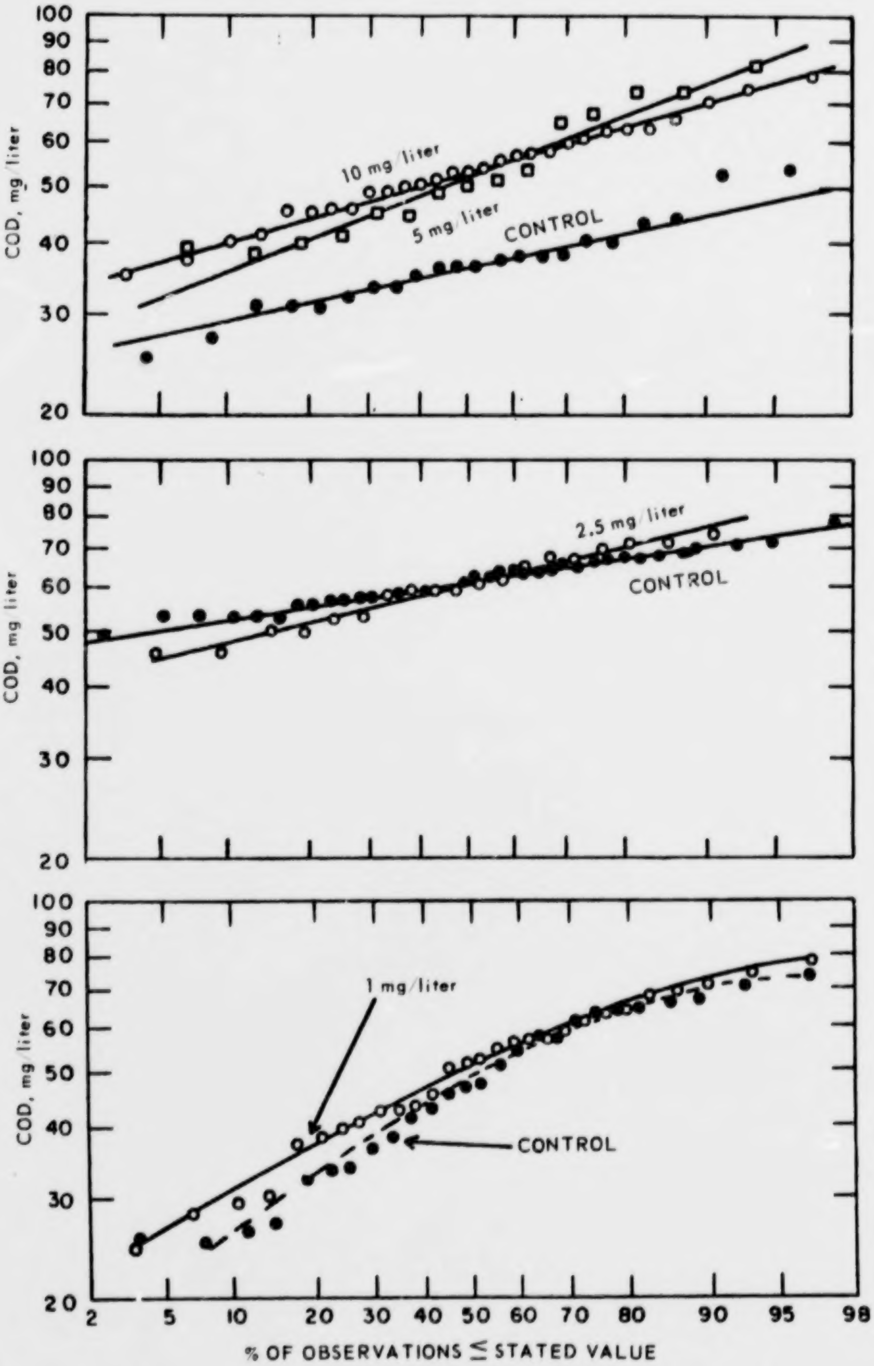

Figure 37. Effect of nickel on COD of final effluents.

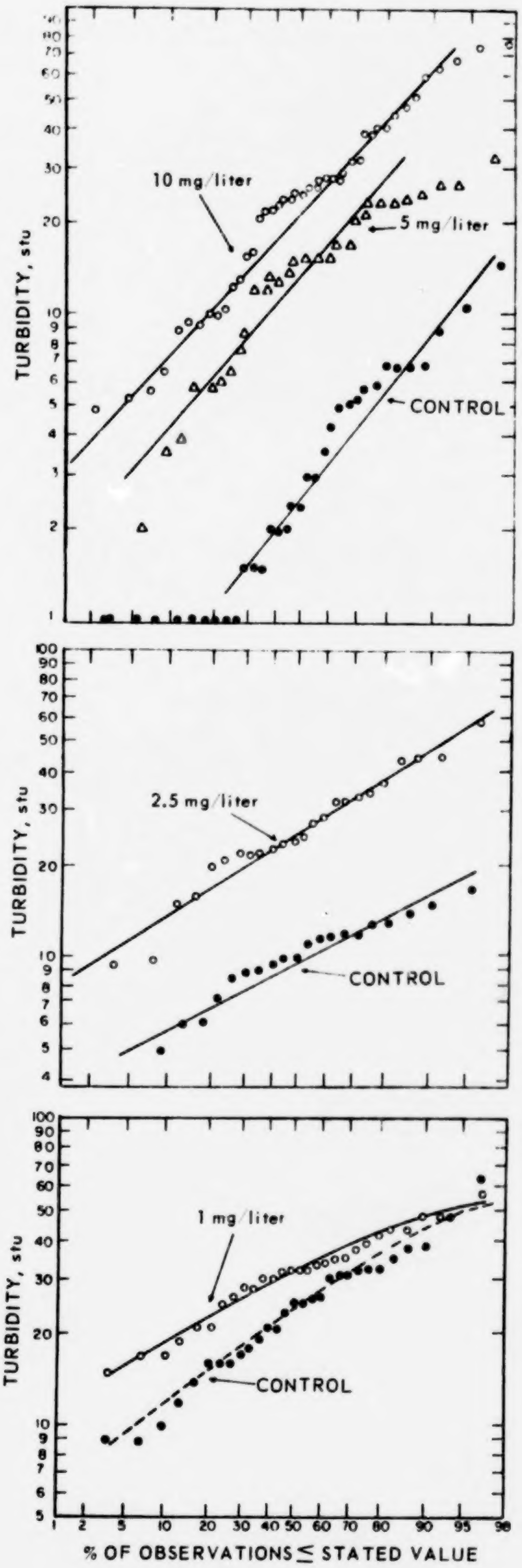

Figure 38. Effect of nickel on turbidity of final effluents.

COD was routinely determined because of the possibility that nickel would inhibit the BOD analysis. In no case was there any indication that such inhibition occurred. Figure 37 shows that 5- and 10-milligram-per-liter concentrations of nickel significantly affect treatment efficiency, based on COD analysis. The COD curves for concentrations of 2.5 and 1 milligram per liter show no significant effect, whereas the BOD curve for the 2.5-milligram-per-liter concentration shows a greater effect than the curve for the 5- or 10-milligram-per-liter concentrations.

The turbidity plots shown in Figure 38 reflect the nickel concentrations in magnitude of effect; each nickel dosage caused impairment of effluent clarity in the order of nickel concentration. Each concentration had a significant effect on turbidity. From the data in Table 34 and Figures 36, 37, and 38, it is concluded that nickel concentrations of 10, 5, and 2.5 milligrams per liter definitely affect the treatment efficiency of an activated-sludge process. The effect of 1 milligram per liter is subtle and is considered near the threshold limit for nickel.

An explanation is not apparent for the anomalous results of the BOD and COD data for the 2.5-milligram-per-liter run, which remain a variant in an otherwise orderly series of observations.

Table 35. NICKEL DISTRIBUTION IN PROCESS OUTLETS

Nickel in sewage, mg/liter	Primary sludge	Excess activated sludge	Final effluent	Imbalance
	Nickel, mg/liter			
10	62	89	72	–
2.5	–	–	1.4	–
1	15	26	0.8	–
	Nickel fed in outlet, %			
10	2.5	14.8	72.1 (52–90)[a]	-11
2.5	–	–	58 (62–80)[a]	–
1	5.4	7.2	72.5 (56–87)[a]	-15

[a] Range of observations.

During the 10- and 1-milligram-per-liter runs the apportionment of the nickel fed among the various sludges and final effluent was traced by material balances. During the 5- and 2.5-milligram-per-liter runs the sampling and analytical program for metal balances was eliminated. The nickel distribution during activated-sludge treatment is given in Table 35. It can be seen that only a small amount of nickel precipitates with the primary sludge. The activated sludge showed no great affinity for nickel; consequently, the major portion of the nickel passed out with the final effluent. The imbalance figure on Table 35 refers to the average degree of success in the balance between the nickel fed and nickel accounted for.

The efficiency of primary and complete activated-sludge treatment in removing nickel from sewage is given in Table 36. Primary treatment in the range studied removes approximately 5 percent of the influent nickel; activated-sludge treatment removes approximately 30 percent of the influent nickel.

Table 36. PERCENT EFFICIENCY OF TREATMENT PROCESSES IN REMOVING NICKEL

Nickel in sewage, mg / liter	Primary treatment, %	Complete activated-sludge treatment, %
10	3	28
2.5	–	42
1	5	28

Table 37. NICKEL CONCENTRATIONS IN EFFLUENTS

Nickel (as$NiSO_4$) in sewage, mg / liter	Primary effluent, mg/liter		Final effluent, mg/liter	
	In solution	Total	In solution	Total
10	–	8.2	–	7.2
2.5	0.9	2.0	1.1	1.4
1	0.78	0.97	0.70	0.75

Table 37 presents the results of analyses for nickel in solution during the 2.5- and 1-milligram-per-liter runs. Grab samples were collected, filtered immediately with a membrane filter, and composited over a 5-day period. The primary effluents have slightly greater total nickel content than nickel in solution; however, the nickel in the final effluent is almost entirely in solution. The decision to classify material passing through the 0.45-micron membrane as soluble was strictly arbitrary. The differentiation of total and soluble metal was made because soluble metal, rather than total metal,

content would be expected to be more indicative of physiological response of recipient organisms, both in the treatment plant and the receiving stream.

Table 38. EFFECT OF SULFIDE ON ACTIVATED-SLUDGE TREATMENT EFFICIENCY OF NICKEL REMOVAL

Period	Average sulfide content of sewage fed, mg/liter	Final effluent ratio: $\frac{\text{total nickel}}{\text{soluble nickel}}$	Efficiency of overall nickel removal, %
1	6	1 1.1 1.1 1.2 1.9	52
2	0.8	1.5 1.9 1.1 1.2	28
3	11	1.3 1	44

Table 38 is a summation of results gathered in an attempt to correlate nickel removals with sulfide content of the sewage fed during the 2.5-milligram-per-liter run. The various sulfide levels were obtained by manipulation of standard pilot-plant operation. Period 1 was the sulfide level normally occurring with routine operation. Period 2 sulfide levels were obtained by mild aeration of the sewage in the holding tank. Period 3 levels were obtained by reserving part of each day's sewage in the holding tank for the next day. From the limited data obtained, no correlation of sulfide content and nickel removal could be deduced, considering the wide variation in efficiency of nickel removal encountered in each of the runs (Table 35).

Slug Dose

The reactions of the activated-sludge process to 4-hour nickel slug doses of 25, 50, and 200 milligrams per liter of sewage were studied. In each case the activated sludge was acclimated to a continuous 2.5-milligram-per-liter nickel dose before the slug-dose test. The logic in using the acclimated system was that routine slight losses are likely to prevail wherever a slug dose occurs.

The slug doses of 25 and 50 milligrams per liter did not impose a very great stress on the system; therefore, only the data obtained during the 200- milligram -per-liter run are presented. Figure 39

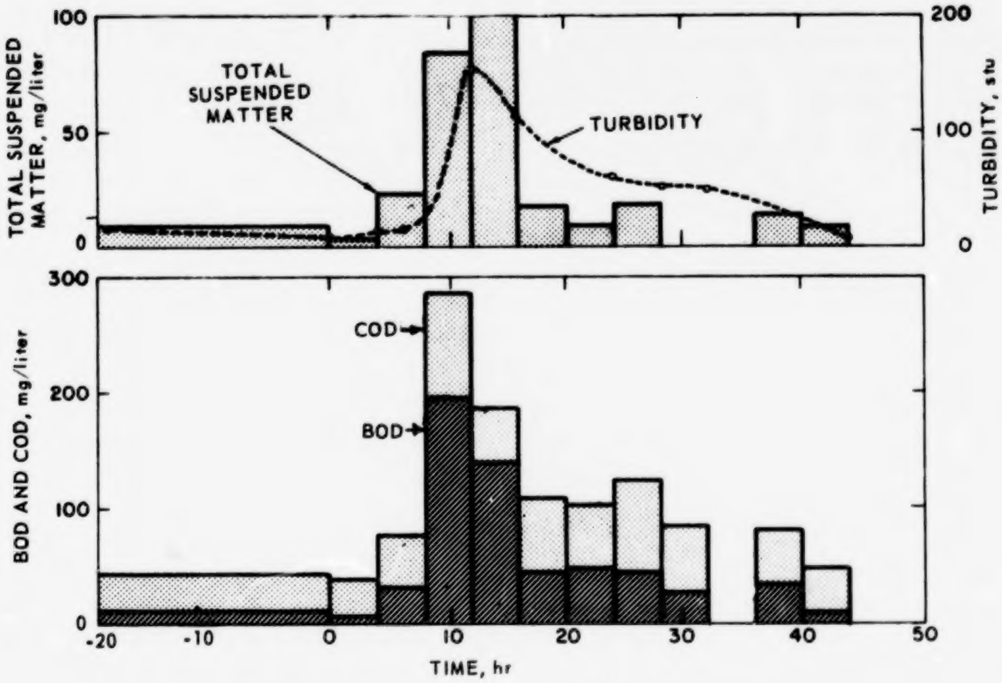

Figure 39. COD, BOD, suspended solids, and turbidity of final effluents, unit fed 200 mg/liter nickel for 4 hours.

depicts the reaction of the activated-sludge process to a 4-hour slug dose of 200 milligrams per liter of influent sewage. The final effluent showed a marked increase in BOD, COD, suspended matter, and turbidity 10 hours after initiation of the nickel slug. These effects diminished in a rather linear manner for the next 30 hours, and the system was producing effluent of preslug quality 40 hours after the slug. This sludge had been acclimated to the continuous 2.5-milligram-per-liter addition, and this addition was continued after the slug dose.

Figure 40 shows the distribution of nickel after the 200-milligram-per-liter slug dose. The nickel concentration reached its peak in the primary effluent in 4 hours and then rapidly decreased; by the end of 8 hours the nickel content was equal to that during the 2.5-milligram-per-liter continuous feed. At the peak of nickel concentration in the primary effluent, 60 percent of the nickel was in solution. The nickel content of the final effluent reached its peak 10 hours after the slug. Eight hours after slugging, 60 percent of the nickel in the final effluent was in solution. After 20 hours, the soluble and total nickel contents were equal. The nickel content of the final effluent gradually dropped to its normal level after 60 hours.

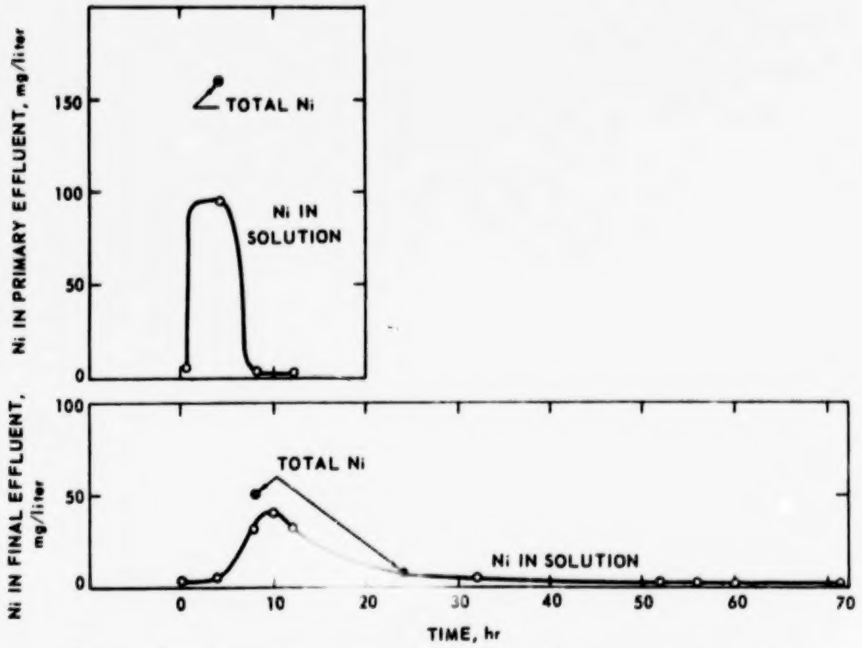

Figure 40. Nickel in primary and final effluents, total and solution; unit fed 200 mg/liter nickel for 4 hours.

NICKEL AND ANAEROBIC DIGESTION

The sludges produced during the 10-milligram-per-liter nickel run were digested anaerobically. A digester fed primary sludge and a digester fed primary and excess activated sludge were studied. These digesters were operated on the nickel-bearing sludge for at least 60 days, almost four detention periods, without any signs of interference with gas production or volatile solids destruction. The gas production averages for weekly periods for the combined primary and excess activated sludge were within the range of gas production of sludges from the control unit.

Since sludges from the 10-milligram-per-liter run did not interfere with anaerobic digestion, primary sludges produced by primary settling of sewages containing nickel doses of 20 and 40 milligrams per liter were studied. The digester receiving sludge from the 20-milligram-per-liter run digested normally for 60 days. At the end of this time the digester was fed sludge produced from sewage containing a 40-milligram-per-liter nickel dose. Digestion proceeded normally for an additional 60-day period. For each anaerobic digestion study, with the exception of the 20-milligram-per-liter run, complete material balances for nickel and solids were obtained. Each sludge added to the digesters was assayed for both total nickel and soluble nickel. Table 39 summarizes the results of the analyses. An interesting feature of these data is that although the sludges fed to the digesters contained considerable nickel in solution, the digested sludges had a very low soluble nickel content. The concentration

Table 39. NICKEL IN SLUDGES

Nickel in sewage, mg/liter	Primary sludge, mg/liter			Excess activated sludge, mg/liter			Digested primary sludge, mg/liter			Digested combined sludge, mg/liter		
	Total	In solution		Total	In solution		Total	In solution		Total	In solution	
		Avg	Range		Avg	Range		Avg	Range		Avg	Range
10	62	9.8	8.3–13.75	8.9	8.9	7.8–11.5	44	1.6	0.7–3.6	70	1.6	0.4–6.5
20	–	12.8	6.2–17.4	–	–	–	–	1.90	–	–	–	–
40	308	13.2	6.8–21.4	–	–	–	277	1.47	0.7–5.0	–	–	–

of nickel reported for digested sludges is an average value after the nickel concentration in the digester had become rather constant.

Table 40 shows the amount of nickel in the sludges, on a dry basis. The purpose of this calculation is to allow comparisons of sludges of various solids contents. The nickel concentrations in the digested sludges can be used to make an approximation of the nickel content of the influent sewage to a plant. The sludge reflects the average concentration of nickel in the sewage over the sludge accumulation period.

Table 40. NICKEL CONCENTRATIONS IN DRIED SLUDGES

Nickel concentration, mg/liter	Nickel in total suspended solids, mg/g			
	Primary sludge	Excess activated sludges	Digested primary sludges	Digested combined sludges
40	8.3	–	15	–
10	2.2	10.6	2.8	7.1
1	1.1	4.6	–	–

During the run with the 200-milligram-per-liter nickel slug dose, primary sludge and a sample of excess activated sludge were collected at peak nickel concentrations and fed to a normal digester. No effect on gas production resulted.

During each anaerobic digestion run a control digester was also operated in parallel with the experimental digester. This digester was operated under identical conditions, but was fed sludges bearing no nickel.

DISCUSSION

This study has demonstrated that the effects of nickel on the activated-sludge process are not linear with concentration, but display decreasing response to increasing concentration. The increased BOD and COD of the final effluents from nickel-fed units, above those of the control units, were about the same for doses of 10 and 5 milligrams per liter. This behavior was noted with chromium (8), copper (16), and zinc (16), all of which have been studied at this laboratory. Biological systems frequently show this behavior, for instance, vitamin and antibiotic assays show linear relationships between dose and effect over only a very narrow range of concentrations.

In the slug dose study, doses of nickel under 200 milligrams per liter did not seriously upset the system. This dose is at least 100 times the amount needed to affect the continuous-dose runs significantly. Even the 200-milligram-per-liter slug dose caused only a temporary decrease in effluent quality, and by the end of 40 hours the system was producing preslug quality effluent.

Table 41. AVERAGE VALUES FOR OVERALL BOD REMOVAL

Continuous nickel concentration, mg/liter	BOD remaining in final effluent, %	Overall removal, %	Reduction in overall removal, %
0	4	96	–
10	7	93	3
0	4	96	–
5	5	95	1
0	5	95	–
2.5	10	90	5
0	12	88	–
1	12	88	0

Table 41 tabulates the overall plant efficiencies based on BOD, for the various continuous nickel-feeding runs. Nickel doses of 10, 5, and 2.5 milligrams per liter had only a slight effect on overall plant performance. No effect on BOD removal was shown by a continuous nickel dose of 1 milligram per liter.

These observations support the conclusion that the aerobic phase of activated-sludge treatment can tolerate, without reduced efficiency, the continuous presence of nickel at concentrations no greater than 1 milligram per liter, but can satisfactorily recover from slugs of at least 200 milligrams per liter.

Primary treatment removed only a small amount of nickel. The majority of the nickel reaching the aeration chamber is passed through to the effluent in soluble form. Complete activated-sludge treatment is approximately 30 percent efficient in reducing the nickel content of influent sewage. Considerations of the effect the final effluent will have on the receiving stream should include the observation that 70 percent of the influent nickel reaches the final effluent.

The possibility of increasing nickel removal efficiency by increasing the sulfide content of the sewage was investigated. The formation of insoluble nickel sulfide was expected to cause the nickel to be sorbed on the biological floc and be removed from the effluent, but the assumption proved unwarranted.

The anaerobic digestion process proved to be very resistant to any effects caused by nickel in the sludges. Digestion of the mixed sludges produced during the 10-milligram-per-liter run proceeded normally. No difficulty with anaerobic digestion of primary sludge produced during the 40-milligram-per-liter run was encountered, nor did a slug of nickel-bearing sludge have a noticeable effect. This nickel-bearing sludge was obtained during a slug dose of 200 milligrams per liter to the sewage feed. An interesting feature of the anaerobic digestion of nickel-bearing sludges is the fact that soluble nickel introduced with the feed sludges is converted to an insoluble form during digestion. The long detention time, high alkalinity, sulfide content, and hydroxyl ion concentration offer a favorable environment for the formation of insoluble nickel compounds.

SUMMARY

Nickel, present continuously, in concentrations ranging from 2.5 to 10 milligrams per liter in the sewage entering a complete activated-sludge pilot plant reduced the BOD removal efficiency a maximum of about 5 percent. Increased turbidity in the final effluent is the most objectionable feature. The maximum level of nickel that will not produce a detectable effect on treatment efficiency was indicated as being greater than 1 and less than 2.5 milligrams per liter.

A 200-milligram-per-liter slug dose of nickel caused a serious reduction in treatment efficiency for a few hours, but the plant returned to normal performance within 40 hours.

Combined primary and excess activated sludge from a plant receiving 10 milligrams of nickel per liter continuously digested satisfactorily. Primary sludge from sewage containing 40 milligrams of nickel per liter digested satisfactorily.

A small percentage of nickel is removed in primary settling. The complete activated-sludge process is about 30 percent efficient in removing nickel. The sulfide content of the influent sewage has no correlation with efficiency of nickel removal.

CHAPTER V. A MIXTURE OF HEAVY METALS*

The effects of copper, chromium, nickel, and zinc introduced individually to the sewage feed of complete activated-sludge pilot plants have been discussed in the previous chapters. The results obtained from the individual studies were used as background information to investigate the effects of a mixture of these four metals on the activated-sludge and anaerobic digestion processes. The plant design and operation can be found in Chapter I.

METAL COMBINATIONS EMPLOYED

The response of the activated-sludge process was measured with each of three metal combinations. The combinations, denoted as MC No. 1, 2, and 3, are given in Table 42. Two of the metals, zinc and copper, were fed as soluble complex cyanides. Chromium (VI) was introduced as potassium dichromate, and nickel, in the form of nickel (II) sulfate.

Table 42. METAL COMBINATIONS USED TO MEASURE RESPONSE OF ACTIVATED-SLUDGE PROCESS

Metal combination	Metal in influent sewage, mg/liter				Total heavy metals, mg/liter	Total CN^- mg/liter
	Copper[a]	Chromium	Nickel	Zinc[a]		
MC No. 1	0.4	4.0	2.0	2.5	8.9	4.3
MC No. 2	0.4	–	2.0	2.5	4.9	4.3
MC No. 3	0.3	–	0.5	1.2	2.0	2.0

[a] Fed as complex cyanides.

Previous studies have shown that once the activated-sludge process acclimates to cyanide, no difference in effects on treatment exists between the metal as a complex cyanide or free cation (13, 16).

Metal combination No. 1 was based on data from the previous studies on the individual metals and represents the approximate threshold limit for each metal. Chromium was deleted from MC No. 2 because chromium at 4 milligrams per liter should have no effect

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*Material in this chapter published previously in *Proceedings of 18th Industrial Waste Conference*, Purdue University. See Reference 30.

on the activated-sludge process (8); therefore, MC No. 2 should show the same reaction as MC No. 1 if there was no interaction of the metals. MC No. 3 was chosen in order to observe miniumum effects and because the ratios of metals reflected average analyses obtained from field samples.

EXPERIMENTAL CONDITIONS

The run in which MC No. 1 was used was divided into two parts. In the first part a supplemented weak domestic sewage was used as sewage feed (8,13,16,17). In the second part a strong domestic sewage was employed with no supplement. The studies with MC No. 2 and MC No. 3 were carried out entirely with the strong domestic sewage.

The sewage was fed from a common storage tank to duplicate pilot-plant units operating at 350 liters per day capacity. One unit received no metal and served as a control. The experimental unit received the combination of metals by constant-head, calibrated, capillary tubes, from which the metal solutions dripped into the sewage feed line immediately ahead of the primary settler. The sewage and metals were added continuously to the units at a constant rate throughout the entire run.

Loading factors for the various unit operations during the aeration phase are given in Table 43. The characteristics of the sewage used during each run are given in Table 44.

Table 43. PILOT-PLANT DESIGN DATA AND LOADING FACTORS

Unit	Loading factor	
Primary settler	Capacity	4.6 gal
	Detention time	1.2 hr
	Surface overflow rate	142 gpd/ft^2
Aeration tank	Capacity	23.6 gal
	BOD loading	0.34 lb/day/1,000 ft^3 aeration tank volume
		0.60 lb/day/lb VS under aeration
	Aeration period	6 hr
Final settler	Capacity	7.9 gal
	Detention time	2 hr
	Surface overflow rate	102 gpd/ft^2

Table 44. CHARACTERISTICS OF SEWAGE FEEDS AND PRIMARY EFFLUENTS FOR CONTROL AND METAL-FED UNITS

Unit	COD, mg/liter		BOD, mg/liter		Suspended solids, mg/liter	
	Primary feed	Primary effluent	Primary feed	Primary effluent	Primary feed	Primary effluent
MC No. 1	463	284	232	145	342	159
Control	366	269	203	140	252	150
MC No. 2	456	275	186	128	350	180
Control	407	284	180	132	269	183
MC No. 3	498	290	243	147	348	155
Control	409	286	223	149	287	158

Each week four 24-hour composite samples of feed, primary effluent, and final effluent from the control and experimental units were analyzed for COD, BOD, and suspended solids. Daily turbidity measurements were made on final effluent grab samples from the control and experimental units. Analyses of total metals at all outlets were performed on 7-day composite samples. Soluble metal analyses were made on daily grab samples that had been filtered immediately through a membrane filter and then composited for 5 days.

The run with MC No. 1 lasted 6 months. The MC No. 2 an No. 3 runs were each of a 3-month duration. All units were acclimated to the experimental feed for 2 weeks before data were collected. Analysis of the final effluent for cyanide, at this time, showed virtually complete destruction of the cyanide.

Details of the anaerobic digestion procedures are given in the literature (18). The loading factors for the digesters are given in Table 45.

Table 45. DIGESTERS, CAPACITY, AND LOADING FACTORS

Digester data	Primary sludge digesters		Primary and excess-activated-sludge digesters	
	Control sludge	Metal-bearing sludge	Control sludge	Metal-bearing sludge
Denoted as	CP	MC No. 1P	CPE	MC No. 1 PE
Capacity, liters	8	8	16	16
Detention time, days	17	17	16	16
Organic loading,[a] lb VS/day/ 1000 ft^3	67	65	37	39

[a] Average loading during test period.

ANALYTICAL METHODS

The procedures used to determine BOD, COD, suspended solids, turbidity, chromium, nickel, zinc, and cyanide have been previously described in Chapters I through IV.

Copper was determined with neocuproine; volatile acids, by the distillation method (tentative); alkalinity, by titration to pH 4.50 with a pH meter; and CO_2, by absorption in 30 percent KOH. These procedures are all outlined in *Standard Methods* (10). The three forms of nitrogen, NH_3-N, NO_2-N, and NO_3-N, were determined also according to procedures in *Standard Methods* (10).

The analytical method for each of the four individual metals in a mixture of metals in sewage and sludges was tested for interference by the method of standard addition. In each case the assay employed proved specific enough to eliminate interference by the other metals in the ranges encountered.

RESULTS

Effects on Aerobic Efficiency

Data from the analyses performed on final effluent samples during the runs were plotted on probability paper as frequency distribution curves. The COD, BOD, and turbidity data for MC No. 1,2, and 3 are given in Figures 41 through 49. Each figure includes data on the proper control unit. Table 46 shows the arithmetic averages of BOD, COD, suspended solids, and turbidity.

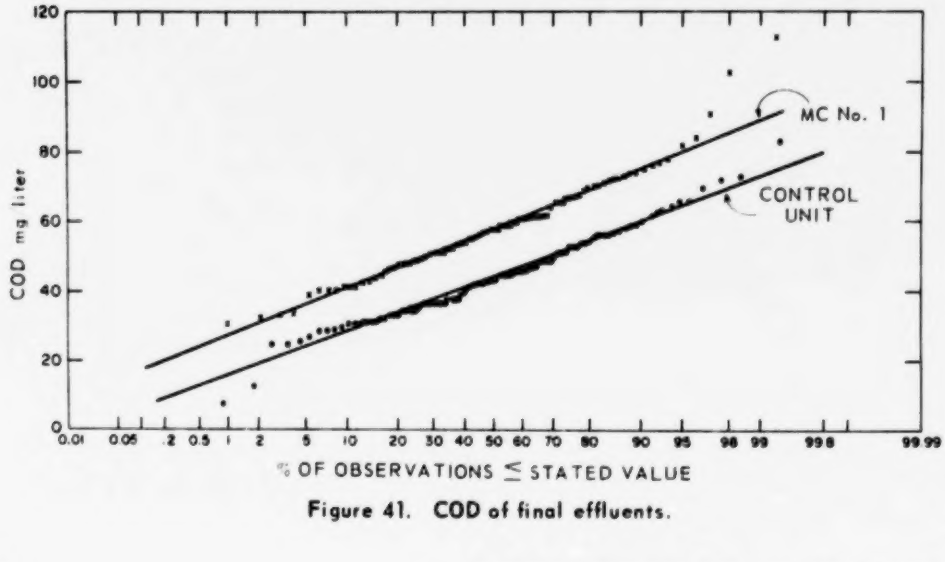

Figure 41. COD of final effluents.

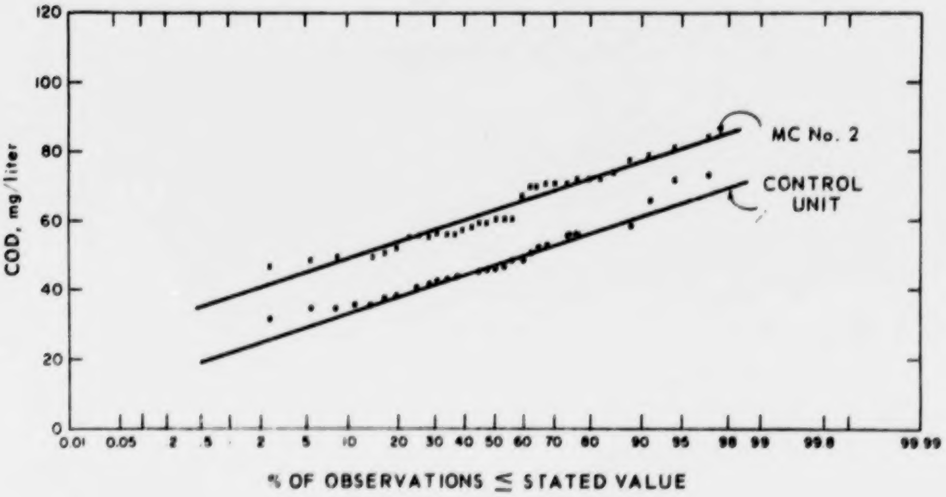

Figure 42. COD of final effluents.

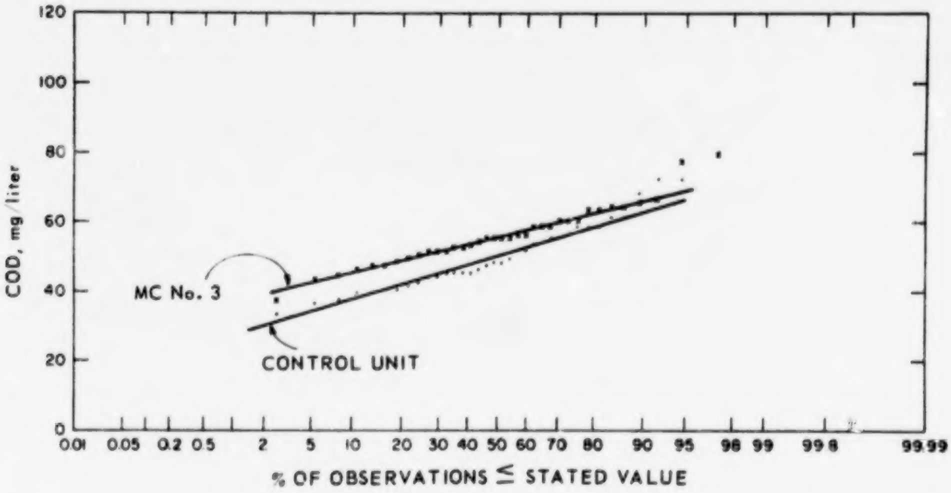

Figure 43. COD of final effluents.

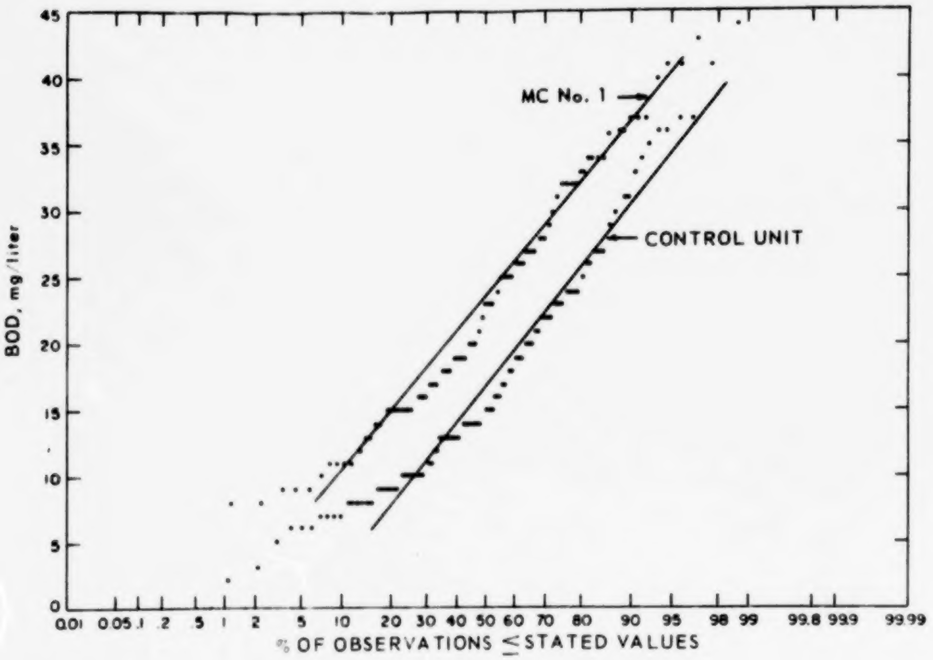

Figure 44. BOD of final effluents.

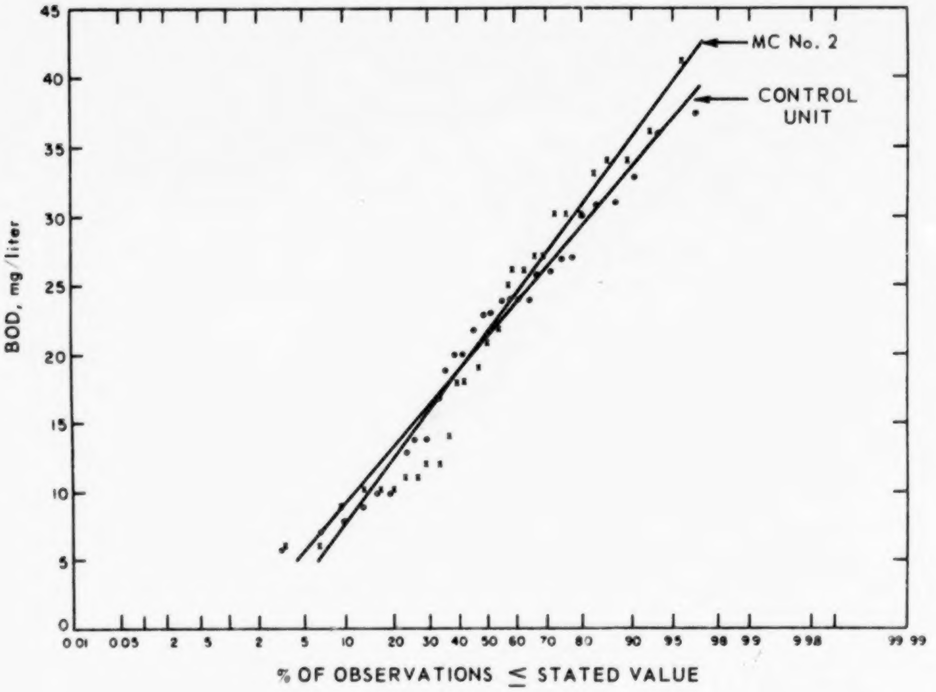

Figure 45. BOD of final effluents.

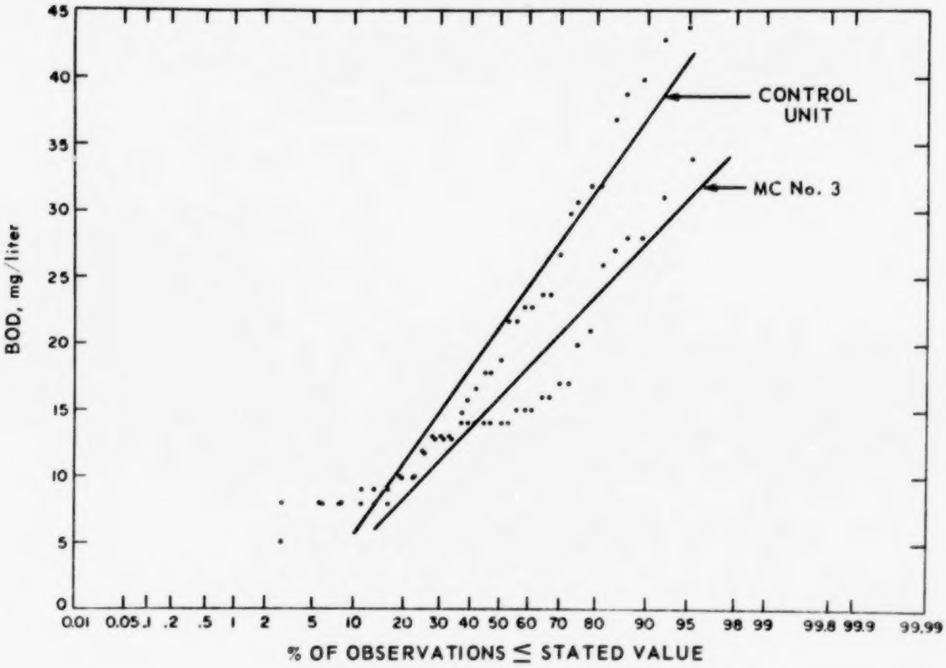

Figure 46. BOD of final effluents.

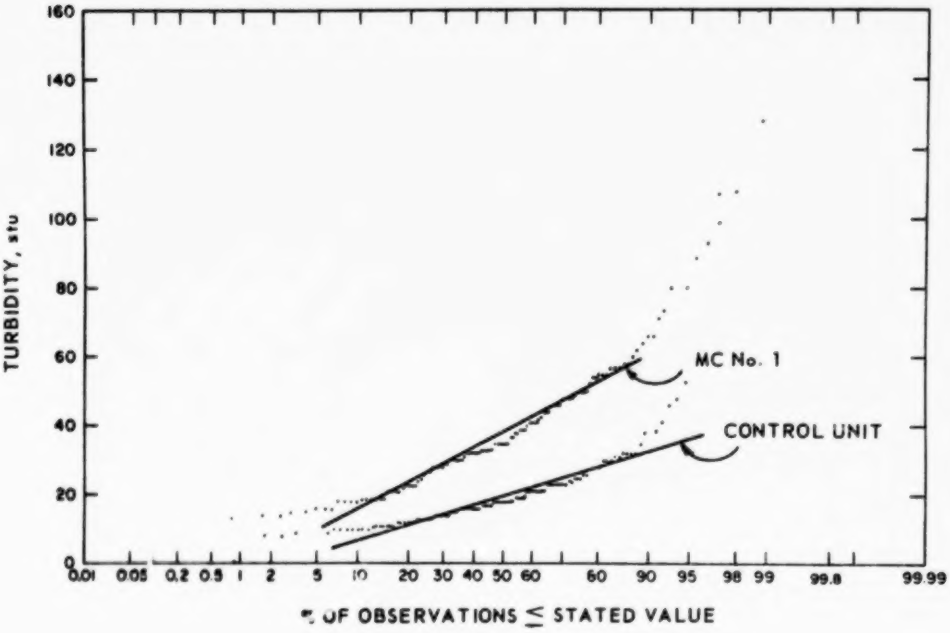

Figure 47. Turbidity of final effluents.

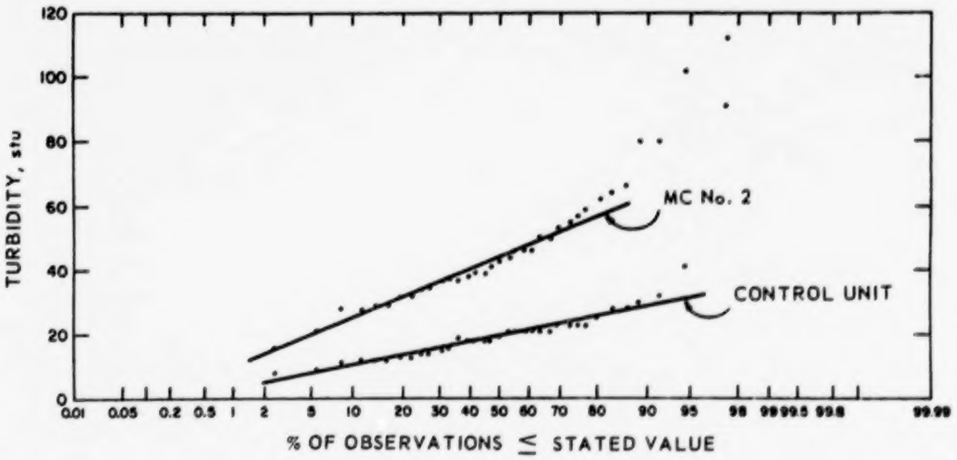

Figure 48. Turbidity of final effluents.

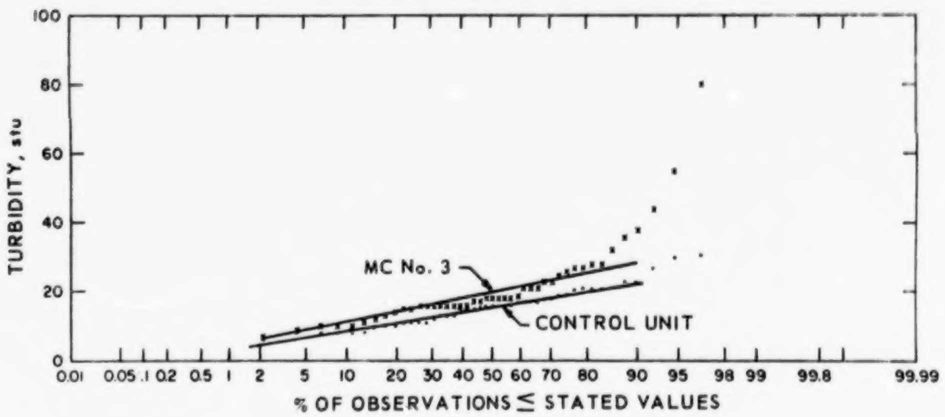

Figure 49. Turbidity of final effluents.

Table 46. CHARACTERISTICS OF FINAL EFFLUENTS FROM CONTROL AND METAL-FED UNITS

Unit	BOD, mg/liter	COD, mg/liter	Suspended solids, mg/liter	Turbidity, stu
MC No. 1	27	66	15	39
Control	18	45	10	26
MC No. 2	21	63	16	74
Control	21	48	13	32
MC No. 3	16	57	9	22
Control	21	52	12	16

These figures and Table 46 show that MC No. 1 and No. 2 had a significant effect on the process; the effect of MC No. 3 combination was of a borderline nature.

The fact that the MC No. 2 BOD data (Figure 45) showed no effect is not surprising. The precision of the routine BOD test is not as good as that of the COD procedure, and small differences in effluent quality may not be apparent from the BOD test. The data on COD, turbidity, suspended solids, and inhibition of nitrification during the MC No. 2 run are sufficient to indicate an overall effect as great as that of the MC No. 1 run.

The effects recorded are significant on the basis of COD, but the overall reduction in plant efficiency for both the MC No. 1 and 2 runs is only about 5 percent. The turbidity curves in Figures 47, 48, and 49 include several points of very high turbidity and, therefore, the entire data did not plot as a straight line. This is due to the occasional receipt in the pilot plants of sewage containing excessive collodial clay turbidity, and the sensitive nature of the turbidity assay.

An interesting observation is that the BOD and suspended solids were actually lower for the MC No. 3 run than for the control unit (Table 46). This may be due to the heavier weight of the metal-fed sludge, resulting in more efficient settling in the final settler. The influence of the metals on sludge density index and volatile solids content of the mixed liquor is shown in Table 47.

Table 47. EFFECTS OF METALS ON MIXED LIQUOR

	Control	MC No. 1	Control	MC No. 2	Control	MC No. 3
Sludge density index	1.5	3.2	1.5	3.4	1.5	2.4
Volatile solids, %	66.7	57.9	66.7	61.8	66.7	63.8

Effects on Nitrification

Three forms of nitrogen were determined on final effluent samples of MC No. 1 and No. 2 runs. The results for the MC No. 1 run are shown in Figures 50, 51, and 52. Similar results were obtained for the MC No. 2 run. Data for the MC No. 3 run were not obtained.

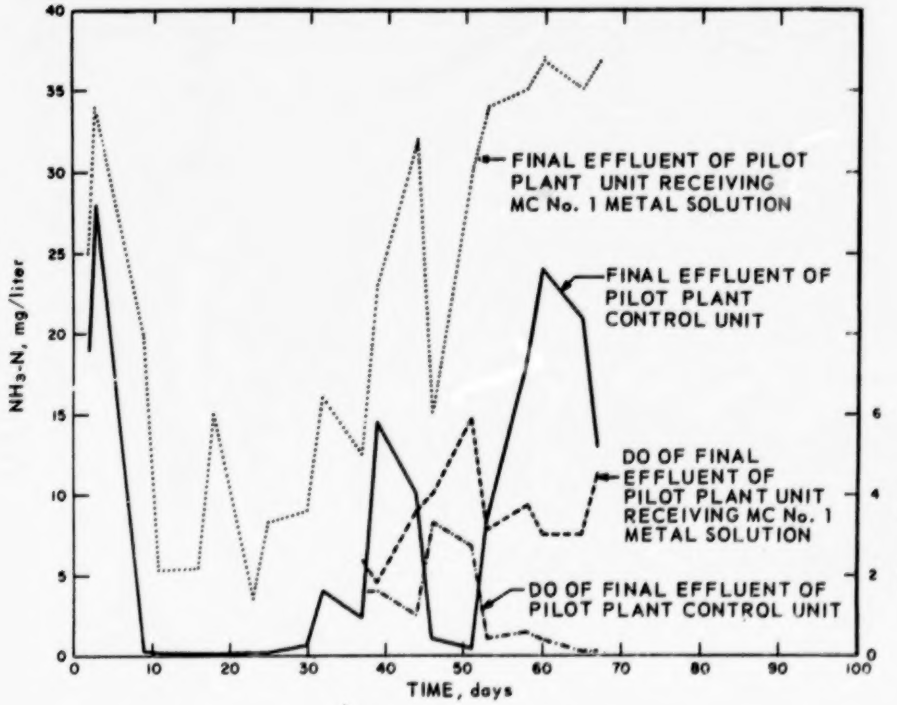

Figure 50. Ammonia nitrogen in final effluents.

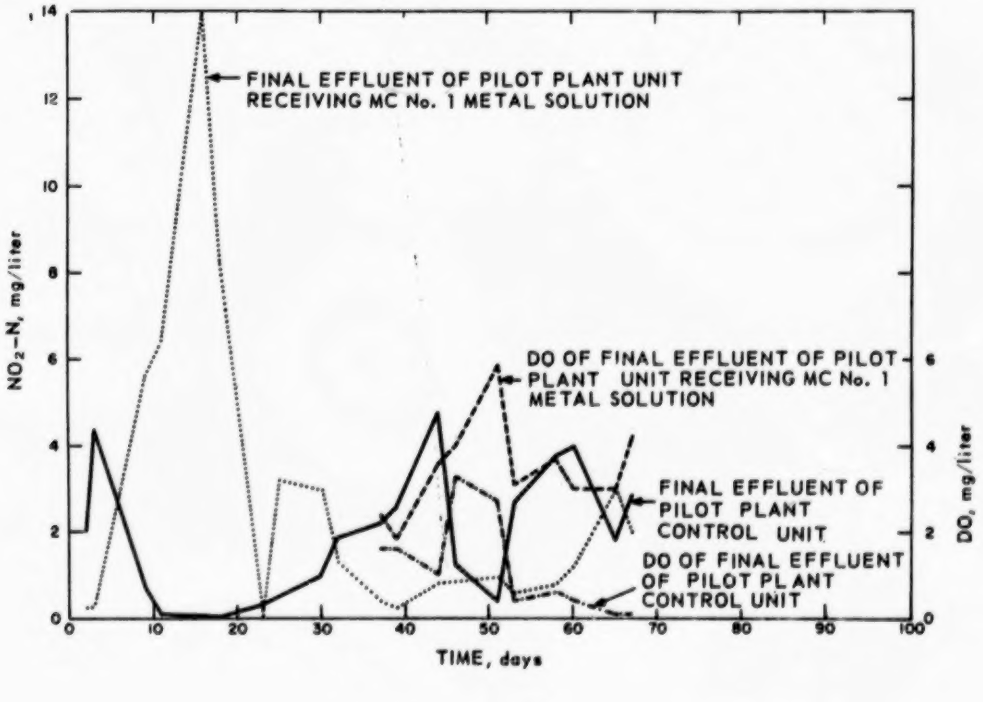

Figure 51. Nitrite nitrogen in final effluents.

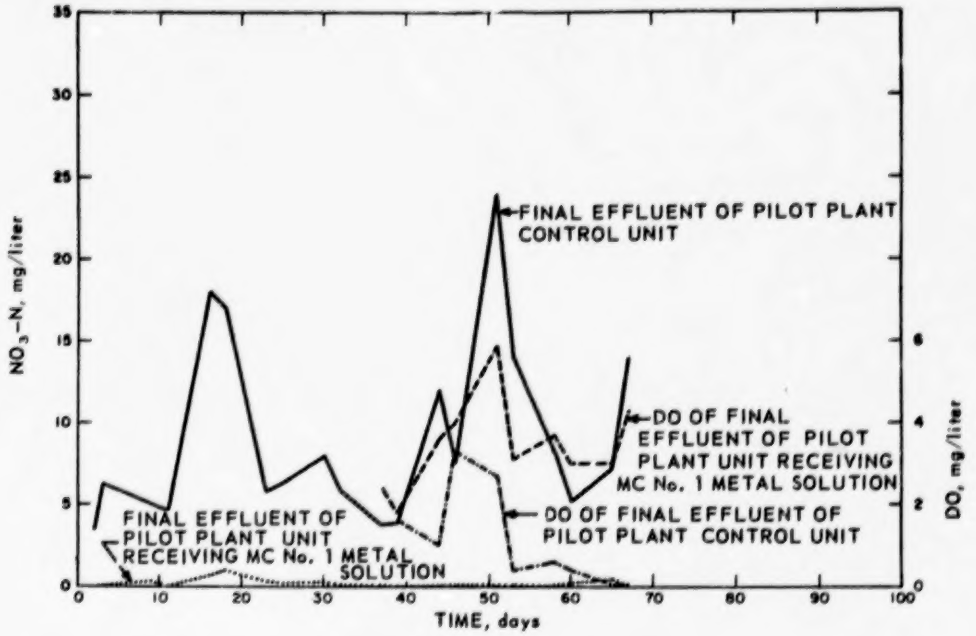

Figure 52. Nitrate nitrogen in final effluents.

Pertinent observations made during the runs with MC No. 1 and 2 are as follows:

1. Ammonia-nitrogen concentrations (Figure 50) in the final effluents of the metal-fed units were consistently higher than those of the control for the same compositing period.
2. Nitrite-nitrogen concentrations (Figure 51) were erratic, particularly in samples from the metal-fed unit, in which they averaged slightly higher than in the control.
3. Nitrate-nitrogen concentrations (Figure 52) in the final effluents of the metal-fed units were usually less than 1 milligram per liter, as contrasted to much higher values found in samples from the control unit.
4. Dissolved oxygen concentrations in the mixed liquors and final effluents of the metal-fed units were consistently higher than those of the control.

The conversion of nitrite to nitrate is virtually completely inhibited, the oxidation of ammonia to nitrite is erratic, and the air requirement of the experimental sludge is not as great as that of the control sludge. Equal amounts of air were introduced to the units through rotometers, and the dissolved oxygen was measured with a galvanic lead/silver probe (19). The presence of dissolved oxygen in the experimental unit indicates that the inhibition of nitrification was independent of oxygen concentration.

Denitrification, with rising sludge, was visually evident in the final settler of the control unit. No such activity was noted in the metal-fed units.

Bozich (20), working with these metals individually, also reported inhibition of nitrification, which appears to be a general symptom of the toxicity of the heavy metals.

Distribution of Metals

Complete material balances for the four metals were performed during the MC No. 1 run. Distribution of the metals in the various process outlets is shown in Table 48. The range of observations show considerable variation in the balance periods; however, the average values agree well with those reported in previous studies of the individual metals.

Table 48. METALS IN PROCESS OUTLETS
MC No. 1

Metal		Primary sludge	Excess activated sludge	Final effluent	Imbalance, %	Overall removal, %	Range of observation, %
Copper	mg/liter	18.2	22	0.22	+ 4	54	32-89
	% of metal fed	19	39.5	45.8			
Chromium	mg/liter	44	97	2.6	-11	37	18-58
	% of metal fed	5.4	20.6	63			
Nickel	mg/liter	9.8	33	1.2	-15	31	12-76
	% of metal fed	2.3	13.3	69.4			
Zinc	mg/liter	59	141	0.26	-12	90	74-97
	% of metal fed	11	67.5	9.7			

The importance of using a complete activated-sludge pilot plant in the study of metal toxicity is shown in Table 49. Two important factors are shown here. First, primary settling reduces slightly the metal burden going to the aerator by removing some metals with the primary sludge. Second, the chemical and physical characteristics

Table 49. EFFECT OF PRIMARY SETTLING ON METALS
MC No. 1

Metal	Soluble metal introduced in sewage, mg/liter	Total metal in primary effluent, mg/liter	Soluble metal in primary effluent, mg/liter
Copper	0.48	0.40	0.22
Chromium	4.1	3.5	3.6
Nickel	2.0	1.6	1.3
Zinc	2.7	2.0	0.15

of the sewage may drastically alter the form of the metal originally introduced. This is emphasized in the case of zinc. Ninety percent of the added soluble zinc is converted to an insoluble form.

These results are similar to earlier observations reported by Masselli (21). Soluble metal is defined in the present study as that portion passing through an HA45 Millipore membrane, followed by acid digestion of the filtrate before analysis. Table 50 shows that metal in the final effluent, with the exception of zinc, is predominantly in soluble form and not associated with the suspended solids fraction.

Table 50. SOLUBLE AND TOTAL METAL CONTENT OF FINAL EFFLUENT
MC No. 1

	Metal, mg/liter			
	Chromium	Copper	Nickel	Zinc
Total	2.7	0.19	1.3	0.26
Soluble	2.4	0.14	0.9	0.04

The average metal content of the mixed liquor during the MC No. 1 run is given in Table 51. If the influent metal concentration

Table 51. AVERAGE METAL CONTENT OF MIXED LIQUOR
MC No. 1

Metal in total solids, wt %				Total metal
Chromium	Copper	Nickel	Zinc	
1.00	0.22	0.33	1.40	3.0

is considered, the mixed liquor has an affinity for the metals in the following order in the system studied: Zn, Cu, Cr, Ni. This affinity reflects accurately the overall removal pattern shown in Table 48.

ANAEROBIC DIGESTION OF SLUDGES

The sludges produced by the control unit and the experimental metal-fed unit, MC No. 1, were digested anaerobically. Both primary and mixed primary and excess activated-sludge digesters were operated for each unit. The mixed digesters received a 3:7 (volume) ratio of primary and excess activated sludge. No difficulties attributable to the metals were encountered. The gas production and metal content for each of the MC No. 1 sludges are shown in Figures 53 and 54 and volatile acids, alkalinity, and pH in Figures 55 and 56. The control digesters, receiving no metal-bearing sludges, gave results almost identical with those shown in the figures. Volatile solids destruction in all cases was satisfactory. Digestion of the MC No. 2 or No. 3 metal-bearing sludges was not studied, in view of the satisfactory digestions of metal-bearing sludges of MC No. 1.

Initially, maintaining both control and experimental digesters on the municipal sewage was difficult because of great fluctuations in

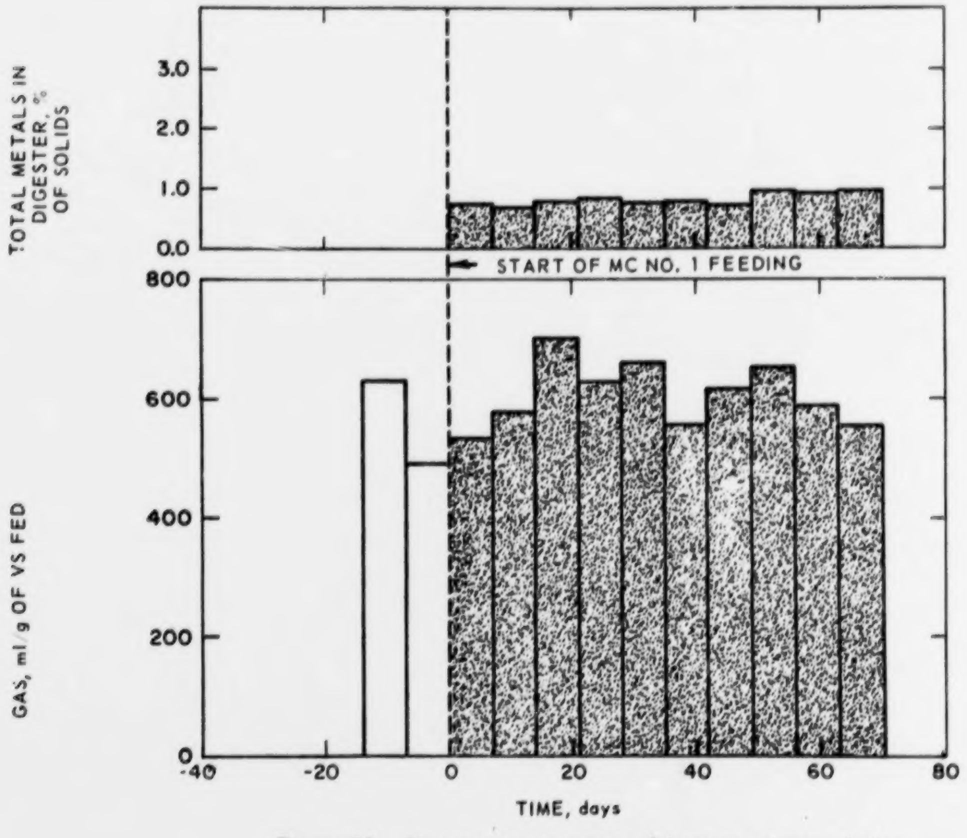

Figure 53. Digester receiving metal-bearing primary sludge.

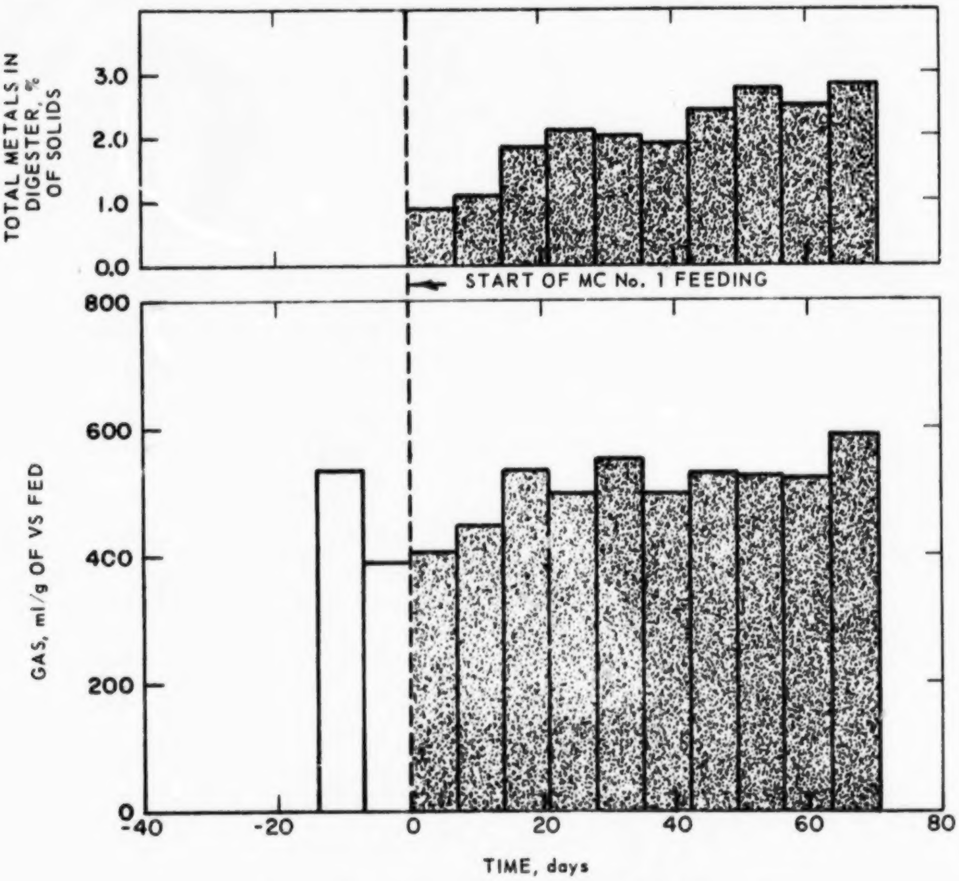

Figure 54. Digester receiving metal-bearing primary and excess-activated sludge.

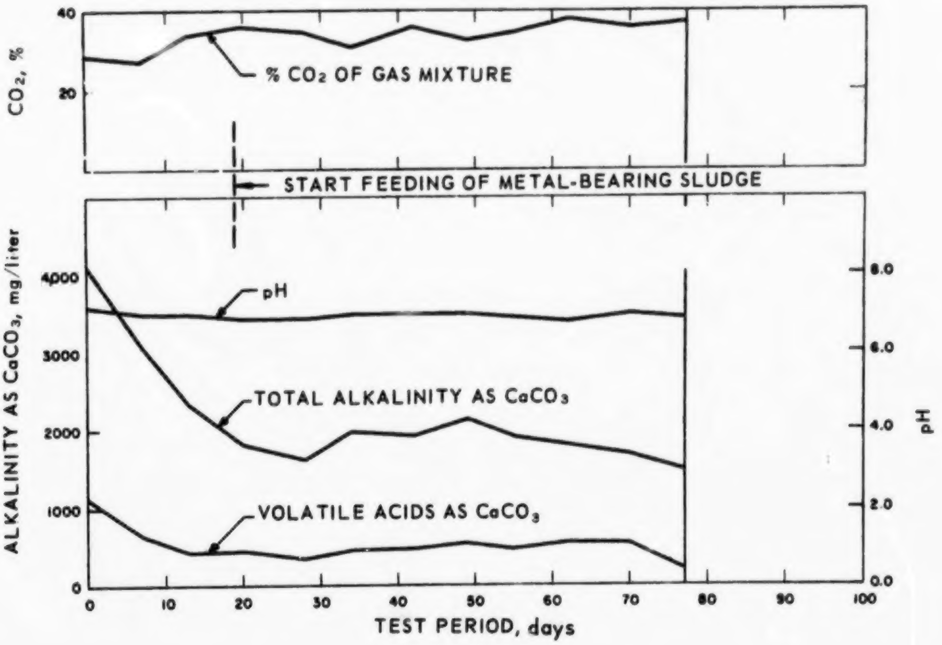

Figure 55. Digester receiving metal-bearing primary sludge.

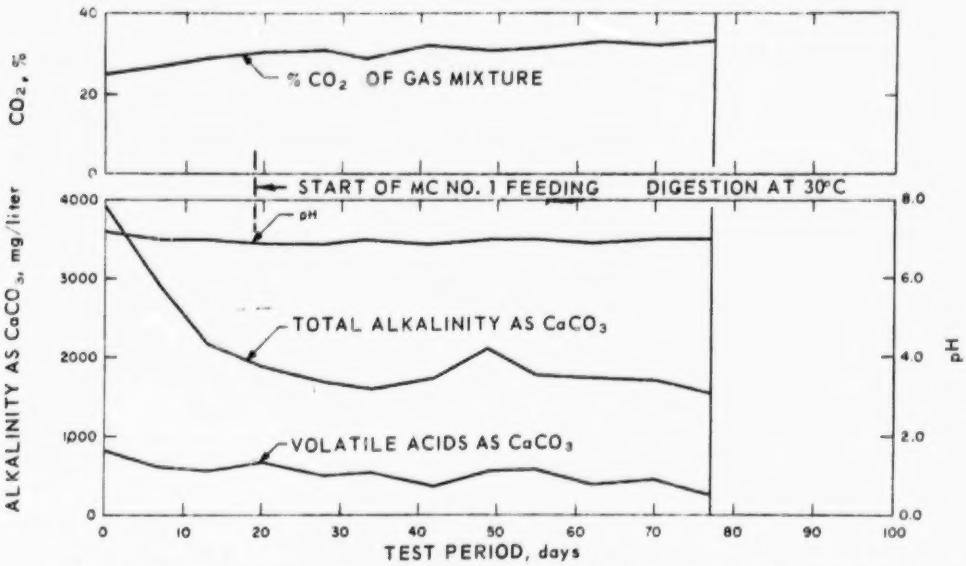

Figure 56. Digester receiving metal-bearing primary and excess activated sludge.

the solids content of the sewage. The problem was solved by adding to the feed sewage a domestic primary sludge from a reserve supply, according to initial daily Imhoff cone measurements of sewage as collected.

The digesters were started with digesting sludge from a municipal primary treatment plant. Figure 53 shows that the initial total heavy-metal content of this sludge was about the same as the metal content of MC No. 1 in the experimental run. Very little change in the total metal content of digested sludge was noted throughout the run. Figure 54 reveals a rising metal content of the digested sludge, eventually leveling off, caused by the higher concentration of metals in the excess activated sludge mixed with the primary sludge. The separate and total metal content of the digested sludges are given in Table 52.

Table 52. TOTAL AND INDIVIDUAL METAL CONTENT OF DIGESTED SLUDGES

MC No. 1	Metal, mg/liter					Total metals, % of solids
	Chromium	Copper	Nickel	Zinc	Total metals	
Digested primary sludge	47.0	18.5	10.2	55	130	0.93
Digested primary and excess activated sludge	88.1	22.3	35.7	122	268	2.73

Each week the digester contents were also analyzed for soluble metals; in no case was the soluble metal content above 1 milligram per liter for any of the four metals. The previous studies of the individual metals had shown that anaerobic digesters are efficient in converting introduced soluble metal to an insoluble form. Coincidental with this finding was the observation that weekly analyses of the digesting sludges for free H_2S* always showed a detectable amount in both the control and experimental digesters.

DISCUSSION

Operation of the two phases in the run with MC No. 1 caused no difference in the distribution of the metals throughout the process or the effect of the metal on the efficiency of treatment. One phase was supplemented with weak domestic sewage, and the other with strong domestic sewage. With the two types of sewage used, the described control pilot plant (8) treated the supplemented weak sewage to 95 percent BOD removal; however, the strong domestic sewage was treated to only 91 percent BOD removal.

Although the effect of the metal dosage in MC No. 1 on treatment efficiency (Figure 41) is significant, it is not striking and is not more than the effect one metal alone would have at this concentration. No synergistic action was found in the combinations employed. MC No. 2 with a total metal concentration of 4.9 milligrams per liter gave an effect as large as that of MC No. 1 with a total metal content of 8.9 milligrams per liter. A previous study (17) showed that both 5- and 10-milligram-per-liter concentrations of nickel gave about the same reduction in efficiency as MC No. 1 and No. 2. This is shown in Figure 57. The nonlinear response with increasing

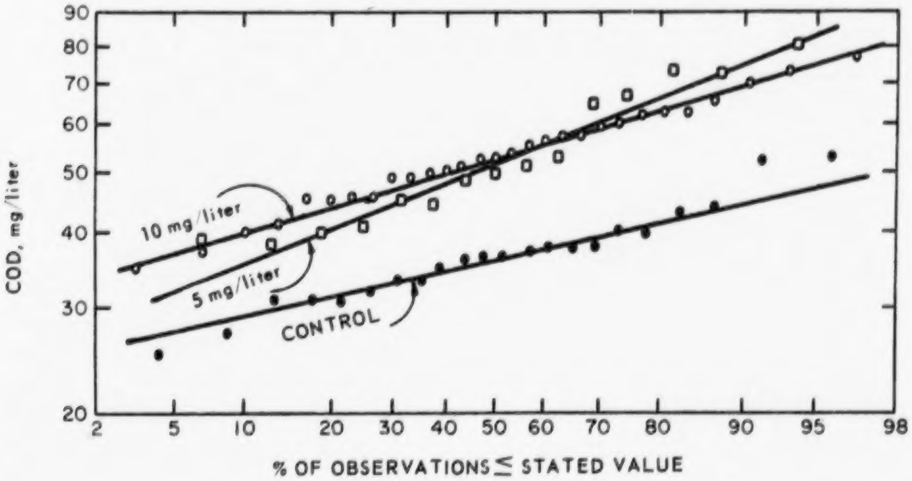

Figure 57. Effect of nickel on COD of final effluents.

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* By evolution with CO_2 into zinc acetate.

metal dosage was also characteristic in the studies on chromium, copper, and zinc (8, 13, 16). MC No. 3 with a mixed metal content of 2 milligrams per liter showed a borderline effect when all the measured parameters were considered.

The nonsynergistic effect of multiple-metal dosage on activated-sludge organisms was recognized by Dawson and Jenkins (22) and Jenkins (23). Tarvin (24) reported no deleterious effects on the aerobic or anaerobic systems of an actual plant receiving heavy metals in concentrations approximating those of MC No. 1 in the present study. The distribution of metals throughout the processes was also similar to that reported here.

The inhibition of nitrification, while only a general symptom of heavy-metal toxicity, is significant because the final effluent from a plant so affected could contain excessive ammonia. A high ammonia content can be a potential toxicant to fish in the receiving stream, create a high chlorine demand if breakpoint chlorination processes are employed, and possibly cause a large oxygen usage because of stream nitrification after dilution.

The oxygen requirement of the metal-loaded system was not so large as that of the control because less oxygen was used for nitrification. Because nitrifying organisms did not acclimatize to the metals during the entire test period, nitrification was never observed in a metal-loaded system.

Material balances and tracking of the metals in the process outlets for the MC No. 1 run agree well with earlier studies of the individual metals, which indicates that there was no appreciable interaction of the metals in combination. Stones, in a series of studies on the distribution of metals in actual treatment plants (25, 26, 27, 28), observed values similar to those reported here. Of the four metals studied, chromium (as chromate) can be expected to be the most variable in efficiency of removal from the influent sewage because the amount of removal is to a large extent controlled by the amount of dissolved oxygen present in the system (8).

Even with complete conventional activated-sludge treatment, considerable metal passes out of the plant with the final effluent. The effects the metal content of the final effluent will have on the receiving stream have not been considered in this study. Pettet (29) has commented on this aspect, but reports no definitive research.

The metal removed from the influent sewage is concentrated in the primary and excess activated sludges. Anaerobic digestion of these metal-bearing sludges produced by the experimental unit was satisfactory. The results were similar to results of previous studies

(8, 13, 16, 17). Anaerobic digestion of sludges is not interfered with when the individual metals Cr, Ni, and Zn are present continuously in the influent sewage at concentrations of 10 milligrams per liter. Copper, continuously present in the influent sewage at a concentration of 10 milligrams per liter, allows normal digestion of primary sludge; difficulty with mixed digestion, however, may occur (18).

SUMMARY

A combination of four metals, with a total concentration of 8.9 milligrams per liter, had no great effect on the overall efficiency of a pilot-scale activated-sludge plant. No synergistic action was noted. No difficulty with the anaerobic digestion of the sludges produced by the plant was encountered. Approximately 90 percent of the zinc, 54 percent of the copper, 37 percent of the chromium, and 31 percent of the nickel were removed from the influent sewage. The metals, in combination, behaved independently in their distribution throughout the process.

Nitrification in the experimental units was almost completely inhibited. This was shown to be a general symptom of heavy-metal toxicity. The ramifications of this inhibition are discussed.

With the exception of zinc, the metals passing through the activated-sludge process and discharged with the final effluent are predominantly in a soluble form. The effects of the metals discharged to the receiving stream were not considered in this study.

CHAPTER VI. SUMMARY OF PILOT-PLANT DATA*

The effects of copper, chromium, nickel, and zinc, individually and in combination, on biological treatment processes studied at the Robert A. Taft Sanitary Engineering Center have been reviewed in the previous chapters. This study resulted from a suggestion by the National Technical Task Committee on Industrial Wastes that the Center study the metallic wastes from the plating industry from the standpoint of their effects on biological treatment.

The work was conducted in pilot plants that were good simulants of a sewage disposal system and were operated under sustained analytical supervision. Sufficient observations were made to establish statistically valid evidence of performance in systems with metal input and metal withdrawal in general working balance. This chapter summarizes these data.

EFFECTS ON AERATION PHASE

To relate results to the metal content of the influent sewage and to duplicate field conditions as closely as possible, a complete activated-sludge pilot plant (Figure 2)was used. The design and loading factors of the pilot plant are representative of many municipal conventional activated-sludge plants. The sewage feed to the plant during the various studies was either a weak supplemented domestic sewage (17) or a strong nonsupplemented domestic sewage. Both type feeds give results indistinguishable by usual analytical measures.

Many investigators of metal toxicity have employed batch operation or direct dosing of the metal to the aeration chamber. Data from individual studies (Table 53) show that primary settling has two effects on the metals before entry into the aeration tank. First, the total metal content of the primary effluent is less than that of the influent sewage, because some metal is removed with the primary sludge. Second, the chemical and physical characteristics of the sewage alter the form of the soluble metal introduced. This was especially true in the case of zinc where 90 percent of the added soluble zinc was converted to an insoluble form. The differentiation of soluble and insoluble metal in all studies was made by filtration

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*Material in this chapter published previously in *Journal Water Pollution Control Federation,* Washington D. C. 20016. See Reference 33.

of the sample through an HA45 membrane filter and by acid digestion of the filtrate before analysis. Masselli (21) working with domestic sewage, reported findings similar to those in Table 53.

Table 53. METALS IN PRIMARY EFFLUENTS

Metal	Soluble metal introduced in sewage feed, mg/liter	Metal in primary effluent, mg/liter	
		Total	Soluble
Chromium (VI)	50	47	38
Copper	10	9	3.0
Nickel	2.5	2.0	1.0
Zinc	10	9	0,6

The procedure used to determine the concentration of metal in the influent sewage that would give a barely detectable reduction in efficiency during the aeration phase of treatment can best be explained by Figure 58, which shows the results of a study of copper

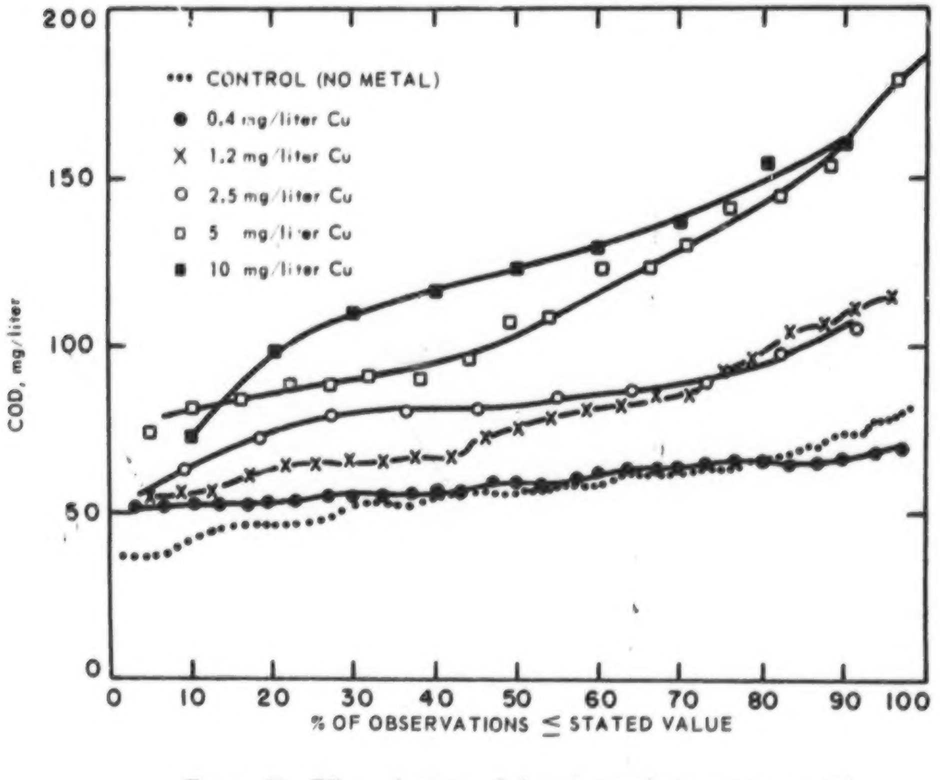

Figure 58. Effect of copper, fed continuously as copper cyanide complex, on COD of final effluents.

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(13). During each run data from an experimental pilot-plant unit and a control unit receiving no metal were compared. The metal was added continuously to a constant sewage feed of the experimental unit. Two weeks of acclimation was allowed before data on the quality of the final effluent were collected. This time interval is also required for the metal content of the activated sludge to build up to a condition of operating equilibrium. Final effluents from both units were assayed daily for BOD, COD, suspended solids, and turbidity. The run for any selected metal dosage was continued for 60 days to obtain sufficient data. The values for the two units were then compared as frequency distribution curves. The parameter of effluent quality in Figure 58 is COD; this is plotted as frequency distribution on arithmetic paper. As shown on the figure copper present continuously at 0.4 milligram per liter did not noticeably increase the COD of the experimental unit. A copper concentration of 1.2 milligrams per liter, however, showed a significant increase in COD. From this and the other parameters measured, copper present continuously at 1 milligram per liter in the influent sewage is concluded to be the threshold dose for the aeration phase.

Another type plot in which frequency distribution curves were plotted on probability paper was found to be useful. Readily available statistical measurements are given by this type plot. If a straight line is obtained with arithmetic probability paper, normal distribution of data is verified. The 50 percent point is very close to the true arithmetic mean of the observations, and the slope of the line is a measure of the standard deviation. Figure 59 is such a plot of data collected during a study of the effects of a mixture of four metals on the activated-sludge process. The need for extensive sampling is shown here. The control unit had an average final effluent COD of

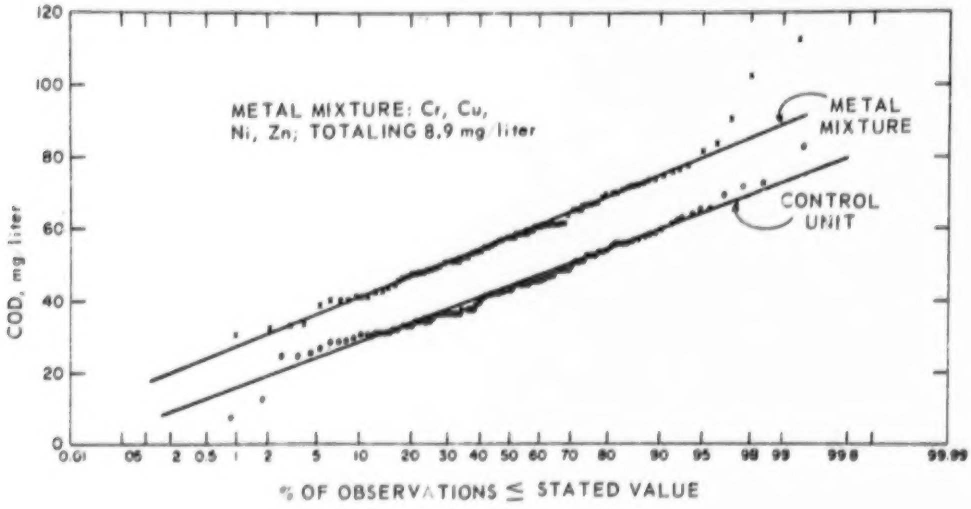

Figure 59. COD of final effluents.

45 milligrams per liter; however, continuation of this point to the experimental unit shows that 12 percent of the time the experimental unit final effluent had a COD of 45 milligrams per liter or less.

Copper and zinc are frequently used by the plating industry as cyanide complexes. These two metals were studied in both the soluble cation form (as sulfate) and as soluble cyanide complexes (13, 16). Results show that once the activated sludge acclimates to the continuous presence of either form of the metal, there is no difference in effects on treatment efficiency. Figure 60-A shows that where turbidity of the final effluent was used as the measure of treatment efficiency, after 8 days the system receiving a 20-milligram-per-liter concentration of zinc cyanide complex had acclimated to cyanide and was producing effluent of stable turbidity. The cyanide content of the effluent followed a similar pattern, with almost complete removal of cyanide at the end of 7 days. Figure 60-B, from a run with a 10-milligram-per-liter concentration of zinc as the sulfate, showed no such acclimation. Direct comparison of the 10-milligram-per-liter concentration of zinc sulfate and a 10-milligram-per-liter concentration of zinc cyanide complex versus the same control unit is shown in Figure 61. The BOD data were collected after 2 weeks' acclimation, and no significant difference between the two forms of zinc exists.

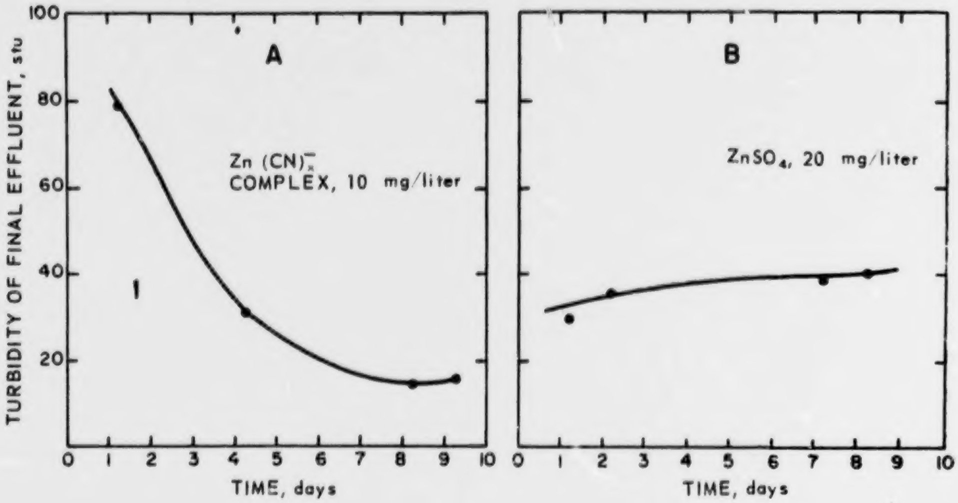

Figure 60. Comparison of acclimation to complexed zinc and zinc sulfate.

The reaction pattern of the activated-sludge process was the same for each of the metals studied. A small dose of metal gives

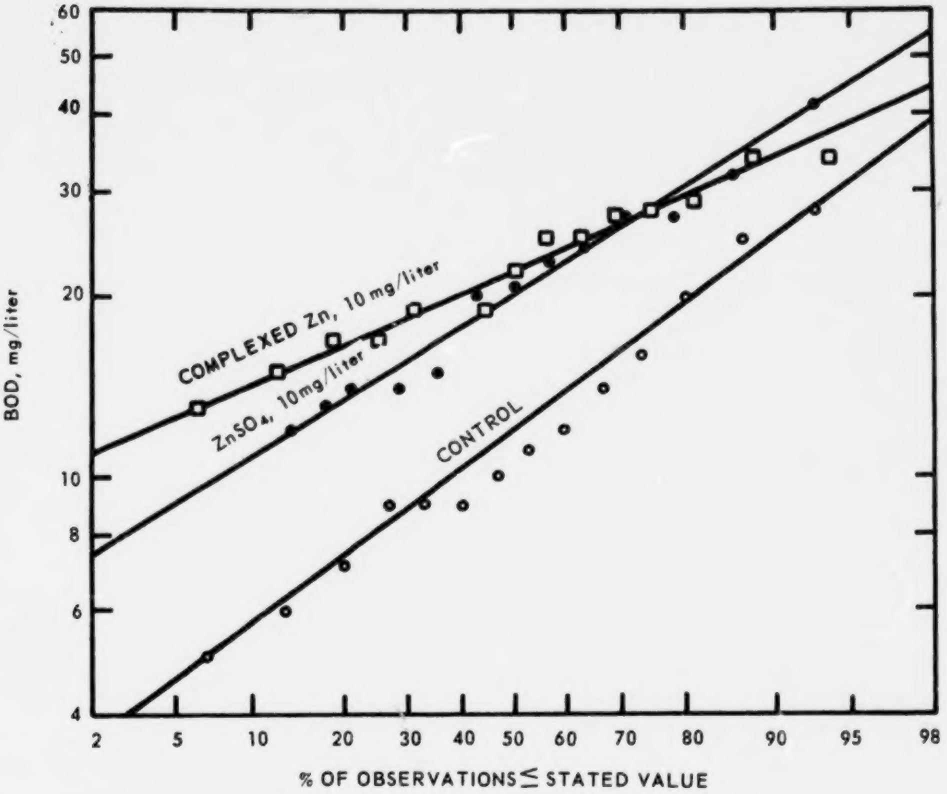

Figure 61. Cumulative frequency data on quality of final effluents with zinc concentration of 10 mg/liter in sewage feed.

a significant reduction in treatment efficiency, but substantially larger doses do not further decrease the efficiency greatly. Figure 62 graphically illustrates this situation.

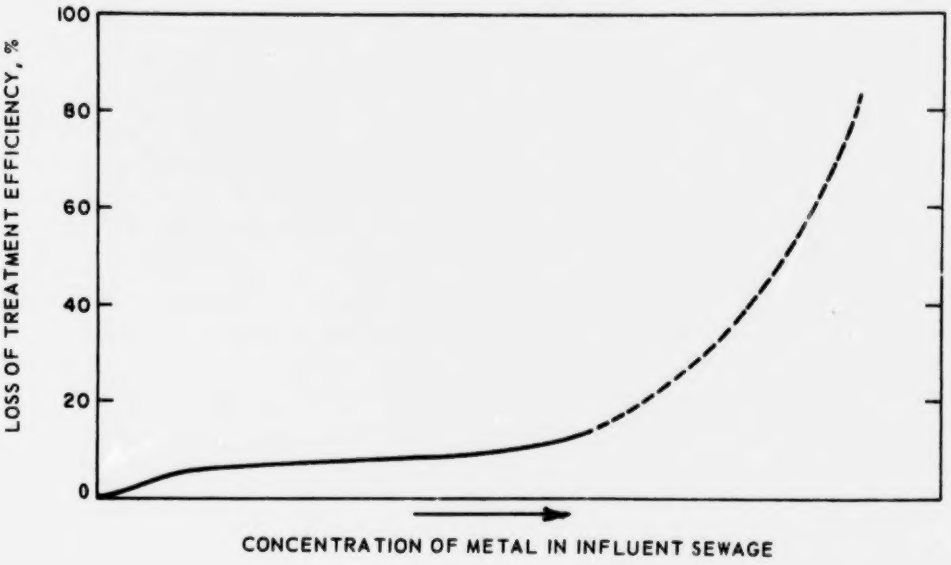

Figure 62. Response of system to metal dosage.

Table 54. CONTINUOUS DOSE OF METAL THAT WILL GIVE SIGNIFICANT REDUCTION IN AEROBIC TREATMENT EFFICIENCY

Metal	Concentration in influent sewage, mg/liter
Chromium (VI)	10
Copper	1
Nickel	1–2.5
Zinc	5–10

Table 54 lists the concentration of metals that give a significant increase in the usual parameters of judging treatment efficiency. These may be considered threshold concentrations; it should be borne in mind, however, that these limits were obtained under carefully controlled laboratory operation. The significance of Figure 62 is that the threshold concentration is mainly of academic interest and actual plant situations are concerned with the plateau region of metal dosage and response.

The results of these studies (30) show that the aeration phase of biological treatment can tolerate in the influent sewage, chromium, copper, nickel, and zinc up to a total heavy-metal concentration of 10 milligrams per liter, either singly or in combination, with about a 5 percent reduction in overall plant efficiency. Tarvin (24) working in municipal plants reported conclusions similar to the above. Dawson and Jenkins (22) from laboratory investigations and Jenkins (23) from field experience also indicate this range of concentration.

Slug doses of metals to the activated-sludge process were also studied. The concentration of metal that constitutes a harmful slug dose is determined by the waste volume, the volume and characteristics of the dilution water, the specific form of the metal, and the usage of the stream below the point of effluent discharge. For convenience only a single measure of effluent quality, such as an increase in organic material passing through the plant, has been used to judge a harmful slug dose. As an example, in Figure 59, the control unit has a COD of 70 milligrams per liter or less 98 percent of the time; then a harmful slug dose can be defined as that concentration of metal that will yield an effluent COD in excess of this value for the subsequent 24 hours of performance. The effects of slug doses were observed on 4-hour metal doses to the influent sewage.

Table 55. METAL CONCENTRATION IN 4-HOUR SLUG DOSE THAT WILL PRODUCE HARMFUL SLUG, AS MEASURED BY COD

Metal	Concentration influent sewage, mg/liter
Chromium (VI)	> 500
Copper	75
Nickel	> 50 < 200
Zinc	160

Table 55 gives the results obtained. To more accurately fix these concentrations would require an inordinate amount of time and expense. Table 55, therefore, is the best estimate of what concentration of metals causes an exceptional displacement of treatment-plant performance as the result of a slug dose.

Not reported in the table are the results of slug studies in which the metals were added as cyanide complexes. In these cases the cyanide toxicity completely obscured the toxic effect of the metal. In general, acclimation of the system to low concentrations of metals or cyanide did not offer protection from slug doses.

The inhibition of nitrification by heavy metals has been previously studied with regard to individual metals (20, 29). A pilot plant that received a combination of four metals also showed inhibition of nitrification. There was no evidence of acclimation of the nitrifying organisms to the metals. The oxygen requirement of this metal-loaded sludge was less than that of the control unit because oxygen for the biological transformation of ammonia to nitrate was not utilized (30). Figure 63 shows the nitrate content of the final effluents of a control and metal-fed unit. Inhibition of nitrification is regarded as an important effect of metal toxicity. A plant so affected would discharge all the influent nitrogen in excess of that needed for synthesis, predominantly in the form of ammonia. Such an effluent would require considerable chlorine if downstream breakpoint chlorination were used, and nitrification in the receiving stream would use large amounts of oxygen.

DISTRIBUTION OF METALS THROUGH THE PROCESS

Complete material balances of the metals were made during each study. Table 56 summarizes these studies. The table is based on the amount of metal fed to a unit during a compositing period. Variation between compositing period was common, as indicated by the range of observations for the efficiency of the process in removing metals. The percent metal unaccounted for in Table 56 is not a firm figure,

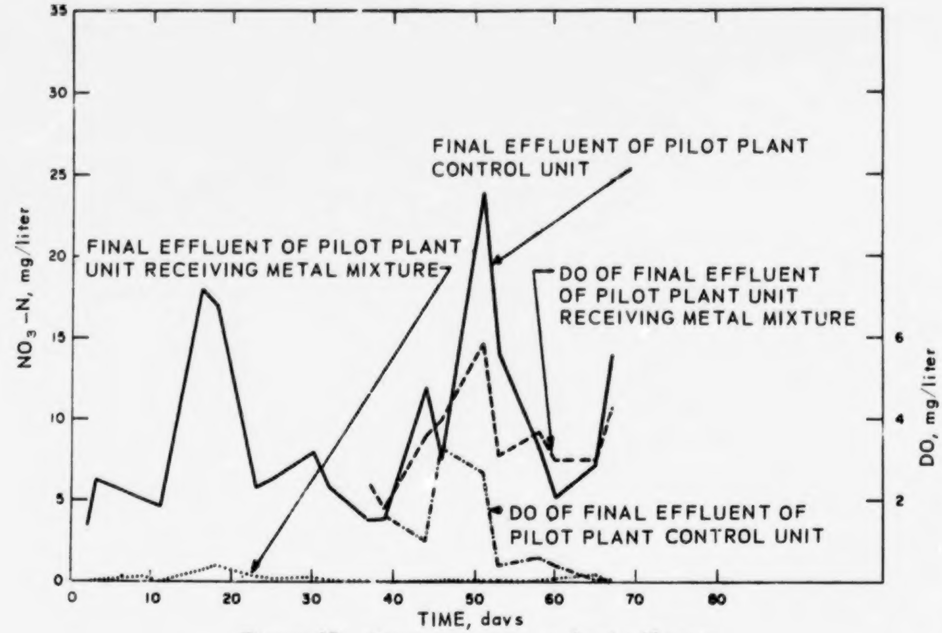

Figure 63. Nitrate nitrogen in final effluents.

Table 56. DISTRIBUTION OF METALS THROUGH ACTIVATED-SLUDGE PROCESS WITH CONTINUOUS DOSAGE

Outlet	% of metal fed			
	Chromium (VI) (15 mg/liter)	Copper (10 mg/liter)	Nickel, (10 mg/liter)	Zinc (10 mg/liter)
Primary sludge	2.4	9	2.5	14
Excess activated sludge	27	55	15	63
Final effluent	56	25	72	11
Metal unaccounted for	15	15	11	12
Average efficiency of process in removing metal	44	75	28	89
Range of observations	18-58	50-80	12-76	74-97

but represents the cumulative errors involved in sampling sludges, flow measurements, and analytical methods.

Metal balances were performed for each selected concentration of the metals studied, not only those shown in Table 56. Each metal was studied in about five increments over the range of 1 to 20 milligrams per liter. In addition, four metals were simultaneously traced during a combination study (30). Over the concentration ranges studied, no great difference in the efficiency of the process in removing the metals was noted. Zinc and copper studied as the cyanide complexes showed the same overall removal as when studied as the sulfates.

Stones, in a series of articles dealing with the fate of copper, chromium, nickel, and zinc through municipal plants (25, 26, 27, 28), records metal removals in general agreement with those reported here. The distribution of metals given by Tarvin is also similar (24).

Chromium, introduced to an activated-sludge process as hexavalent chromate, can show wide variation in concentrations at the various process outlets. Reducing substances in the raw sewage can cause precipitation of trivalent chromium with the primary sludge. Also, under anaerobic conditions the organisms in the return sludge entering the primary settler can utilize the oxygen of the chromate radical and adsorb the trivalent chromium on the biological floc (8). Under these conditions chromium removal can reach 90 percent.

Table 56 shows that a considerable portion of the metal introduced is removed in the secondary sludge. The effects of the metals on the mixed liquor are apparent even in the 1- to 2-milligram-per-liter range. During 5 years of study no bulking was encountered in a metal-fed system. The floc in the final settler quickly settled. Control units frequently bulked. Table 57 shows the effects of a combination of four metals on the sludge density index and volatile solids content of mixed liquor.

Table 57. EFFECTS OF METALS ON MIXED LIQUOR SOLIDS

Analysis	Mixed liquor from			
	Control unit	Metal mixture		
		8.9 mg/liter	4.9 mg/liter	2.2 mg/liter
Sludge density index	1.5	3.2	3.4	2.4
% volatile solids	66.7	57.9	61.8	63.8

With the exception of zinc, the conventional activated-sludge process is not very efficient in the removal of metals from the influent stream. The metal removed is concentrated at two points. In the primary sludge, a maximum concentration would occur if all the metal were removed with this sludge. Here the ratio of total flow volume to primary sludge volume is a limiting factor. Another point of concentration is in the secondary sludge. Since the volume of secondary sludge removed from the process may be small compared to the flow through the process, concentration may be high at this point.

There is no net removal of metal if the primary and secondary sludges containing the metals are not permanently removed from the line of flow. For instance, an extended aeration plant passes all the metal to the receiving stream unless secondary sludge is removed.

The copper, chromium, and nickel discharged with the final effluent from an activated-sludge plant receiving these metals are predominantly in a soluble form. At an influent concentration of 10 milligrams per liter, only a small amount of zinc is discharged, and this is an insoluble zinc. At higher influent concentrations greater amounts of zinc are discharged as soluble zinc (16).

EFFECTS ON ANAEROBIC DIGESTION

The metal-bearing sludges produced by the pilot plants were digested in single-stage nonmixed digesters. Organic loading was for nonmixed operation. A small circulating pump was used once each day to obtain representative samples of sludge for material balances. In each metal study both primary sludge and combined primary and secondary sludges were digested (18). The metal content of the sludges fed to the digesters during several of the runs is given in Table 58. The primary sludges were about 2 percent solids, and the secondary sludges, about 0.5 percent solids during these studies. On a percentage-of-solid basis, the metals in the secondary sludge are concentrated to a much greater extent than in the primary sludge.

Table 58. METAL CONTENT OF SLUDGES FED TO DIGESTERS

Metal	Continuous dose in influent sewage, mg/liter	Primary sludge, mg/liter	Excess activated sludge, mg/liter
Chromium (VI)	50	330	530
Copper	10	280	160
Nickel	10	62	89
Zinc	10	375	328

A digester receiving combined sludges will contain more metal on a percent-of-solids basis than a digester receiving primary sludge, when operated at the same influent sewage metal concentration. Digester failure due to heavy metals occurs at a lower influent metal concentration in a combined-sludge digester than in a primary-sludge digester (18).

The maximum continuous influent sewage metal concentrations for satisfactory anaerobic digestion are given in Table 59.

Table 59. HIGHEST DOSE OF METAL THAT WILL ALLOW SATISFACTORY ANAEROBIC DIGESTION OF SLUDGES CONTINUOUS DOSAGE

Metal	Concentration in influent sewage, mg/liter	
	Primary sludge digestion	Combined sludge digestion
Chromium (VI)	>50	>50[a]
Copper	10	5
Nickel	>40	>10[a]
Zinc	10	10

[a] Higher dose not studied.

The response of the anaerobic system to metal dosage does not exhibit a plateau region as does the aeration phase; it is an all or none reaction. Digestion either proceeds normally or ceases entirely. This may be more apparent than real, however, because the analytical measures of assessing digester performance are not as direct as those for the aeration phase.

The results of these metal studies show that in the cases of chromium, nickel, and zinc an influent sewage metal concentration of 10 milligrams per liter, either singly or combined, will not affect digestion. Copper continuously present at 10 milligrams per liter causes failure of combined-sludge digestion.

The prevailing conditions of anaerobic digestion are such that soluble metal introduced with the feed sludges is efficiently converted to an insoluble form. This is shown in Table 60.

During these studies no correlation of digester failure with soluble metal in the digesting sludge could be found. The soluble sulfide content of digesting sludge offered no direct measure of the digester's ability to tolerate metals.

Table 60. SOLUBLE METAL CONTENT OF SLUDGES COMPARED WITH TOTAL METAL CONTENT OF DIGESTED SLUDGE

Metal	Concentration in influent sewage, mg/liter	Soluble metal			Total metal
		Feed sludges		Digested combined, mg/liter	Digested combined, mg/liter
		Primary, mg/liter	Excess activated, mg/liter		
Chromium (VI)	50	38	32	3	420
Copper	10	2	0.5	0.7	196
Nickel	10	10	9	1.6	70
Zinc	10	0.3	0.1	0.1	341

A few slug doses to anaerobic digesters were studied. The slugs to the digesters were in conjunction with the aeration slugs. The sludges produced by the activated-sludge process during a metal slug were collected and fed to satisfactorily operating digesters. In no case was there any interruption of digestion caused by the metal-bearing sludges. Concentrations of metals in the influent sewage during these slug studies are given in Table 61.

Table 61. DIGESTERS FED COMBINED SLUDGES PRODUCED DURING METAL SLUG TO ACTIVATED-SLUDGE PLANT

Metal	Concentration of metal in sewage feed, mg/liter	Effect on digestion
Chromium (VI)	500	None
Copper	410	None
Nickel	200	None

More-detailed studies were not conducted because the logistics of digester operation make it unlikely that an operating digester would be upset by the sludges produced during a slug period. This belief is based on the facts that a digester is not on the main flow stream and only a small part of the total flow through the plant reaches it, and the daily additions to a digester are only a fraction of the total digester volume.

SUITABILITY OF FINAL EFFLUENT

These studies have dealt with the effects of metals on the biological sewage treatment processes; however, with the increasing reuse of surface water, the metal content of the final effluent becomes important. Pettet (29) and Ettinger (31) have commented on this point. Table 62 shows that each of the ions considered in our metal studies have definite maximum limits either for drinking water or protection of game fish.

Table 62. RECOMMENDED MAXIMUM CONTENT OF METALLIC TOXICANTS AND ASSOCIATED IONS

Ion of interest	Maximum concentration, mg/liter	
	For drinking water	For game fish[a]
Chromium (III)	–	1[c]
Chromium (VI)	0.05[b]	20[c]
Copper	1.0[b]	0.04[d]
Nickel	–	0.8[c]
Zinc	5.0[b]	0.8[d]
Cyanide	0.01[b]	0.02[d]
Ammonia, free	0.5[e]	2[d]

[a] The values given for game fish may not be pertinent to any given situation, since there are wide ranges of values depending upon the characteristics of the water, aquatic species involved, and chronic versus acute exposure conditions. (Post-publication comment)

[b] Recommended by USPHS Drinking Water Standards (1962).

[c] Estimated from data presented by Doudoroff and Katz, *Sew. and Ind. Wastes* 25:802. (1953).

[d] Estimated by C. M. Tarzwell, Robert A. Taft Sanitary Engineering Center.

[e] International Commission.

The importance of considering the metal content of the final effluent is illustrated by chromium. Moore (8) pointed out that 10 milligrams per liter would not interfere with conventional activated-sludge treatment or anaerobic digestion of the sludges and that about 50 percent of the metal would reach the final effluent. Chromium at this concentration would be acceptable from the standpoint of plant performance; however, the low concentration of chromium allowable in drinking water indicates that if downstream use of the final effluent from a plant receiving a 10-milligram-per-liter concentration of chromium was for this purpose, considerable dilution would be required before the supply would be acceptable.

DISCUSSION

The results of these studies show that for each phase of treatment, aerobic, anaerobic, and discharge of final effluent, there are different bases for judging the concentration of metals acceptable in the influent sewage.

The plateau-type response of the aeration phase shows that concentrations of metal many times higher than the threshold concentration can be received without greatly reducing efficiency. In a situation in which removal of organic matter is not critical, the most sensitive performance criterion may be the ability of the digester to handle the sludges produced. Since there are alternatives to anaerobic digestion, this need not be a bottleneck.

In other cases the amounts of metals passing through the plant to the receiving stream may be the factor that determines the concentration of metals permissible in the plant influent.

CHAPTER VII.

HEAVY METALS IN WASTE-RECEIVING SYSTEMS*

In zones of concentrated population in inland areas, industrial and domestic waste water enters a system that automatically places this discarded material where people must use it again. This system started out very primitively with the invention of water-borne disposal, but the amount of waste water reconditioning included in the system is continually increasing, essentially because it must.

The most common elements of a contemporary waste-water transportation and reconditioning system are shown schematically in Figure 64. Clearly the inland sewage treatment plant is only one

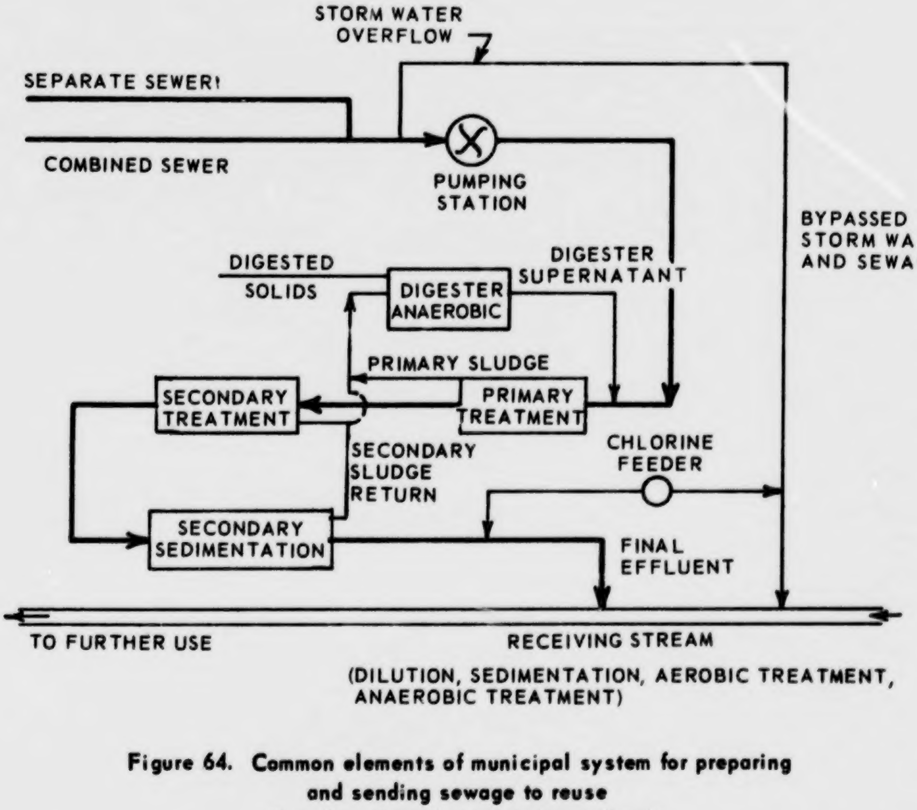
STORM WATER OVERFLOW
SEPARATE SEWER
COMBINED SEWER
PUMPING STATION
BYPASSED STORM WATER AND SEWAGE
DIGESTED SOLIDS
DIGESTER ANAEROBIC
DIGESTER SUPERNATANT
PRIMARY SLUDGE
SECONDARY TREATMENT
PRIMARY TREATMENT
SECONDARY SLUDGE RETURN
CHLORINE FEEDER
SECONDARY SEDIMENTATION
FINAL EFFLUENT
TO FURTHER USE
RECEIVING STREAM
(DILUTION, SEDIMENTATION, AEROBIC TREATMENT, ANAEROBIC TREATMENT)

Figure 64. Common elements of municipal system for preparing and sending sewage to reuse (Main flow channel shown in heavy lines).

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*Paper presented at Interdepartmental Natural Resources Seminar, Columbus, Ohio, March 1963. See Reference 31.

of the way stations along a system that converts waste water into a portion of a general-purpose water resource to furnish water for the following missions:

1. Drinking and culinary purposes.

2. Recreation and aesthetic enjoyment.

3. Work.

Examples of work performed by water include such domestic chores as flushing the toilet or conveying ground garbage from the home, and the complete array of industrial water usages including irrigating, cooling, industrial processing, growing fish for commercial harvesting, generating power, and economical moving of freight.

Many characteristics of waters receiving wastes are altered by contaminants brought in by treated waste water. In the case of the metallic wastes, factors requiring examination include the effects of the metallic element or compound on the utility of receiving water for growing fish or for reconversion to drinking water. Measures of water quality required or recommended for drinking water and estimates of the quantities of metals tolerated by desirable fishes are shown in Table 62. Values such as those cited define permissible boundaries where treated and diluted mixtures of sewage and metallic wastes enter multifunctional bodies of water.

The literature contains a mass of conflicting information based largely on shallow academic studies and fragmentary observation by disposal plant operators. Answers were desired concerning the amounts of metallic wastes that could be regularly discharged as a normal part of manufacturing operations. In addition, there was general interest concerning the effect of sudden slug doses such as those that result from manufacturing accidents or haphazard dumping. Our task clearly was to operate a good simulant of a sewage disposal system under close and sustained analytical supervision, and to make sufficient observations to establish statistically valid evidence of performance in systems with metal input and metal withdrawal in general working balance. In some cases there was need for studying both simple salts and cyanide complexes of the metals of interest.

As stated previously, the objectives of our studies have been:

1. To determine the extent to which sewage treatment processes can tolerate metallic wastes without losing efficiency in their treatment of organic pollutants in sewage.

2. To determine the extent of removal of metallic wastes in sewage treatment plants and to follow their travel and concentration in various conventional sewage process units.

3. To develop modifications of sewage treatment procedures that will make them more tolerant of metallic wastes or more efficient in the removal of metals from sewage.

Additional objectives now include study of the effects of various metals on nitrogen transformations, and the determination of the effects of ratios of organic load to metal content on activated-sludge behavior.

Some of the characteristics of the system that receives, and reconditions, waste water and submits it for reuse are shown in Table 63. Metals may be exposed to reducing conditions and to sulfides in the sewer, pumping stations, primary treatment tanks, sludge thickeners, and even secondary treatment units as well as the anaerobic digester. As will be pointed out later, we have found reduction and sulfide formation important in determining the interaction of metals and treatment processes.

Table 63. CHARACTERISTICS OF SEWAGE COLLECTION, TREATMENT, AND REUSE SYSTEMS

Element	Common ranges of time in transit	Environmental characteristics	Remarks
Collection system	0.2–24 hr	Aerobic and anaerobic, 2 ft/sec velocity. Movement may be intermittent.	Sulfides frequently generated, at least in portions of system.
Primary treatment	0.5–3 hr	Anaerobic frequently, although it may be aerobic. Both conditions may occur on 1 day.	May be omitted or very brief, ahead of activated-sludge treatment
Secondary treatment	1–12 hr	Aerobic with limited but important micro and macro anaerobic environments.	Likely to concentrate biologically resistant materials by inclusion and adsorption.
Anaerobic digestion	7–28 days	Anaerobic	May eventually be superseded as a frequent system component.
Receiving water	Reuse may start immediately	Hopefully, aerobic; may be aerobic with anaerobic bottom areas.	Drinking water has been based on water from sewage given multiple recycling.

The pilot plant operated has been described in some detail in Chapter I. The aerobic part of the system consists of a reservoir of sewage, metal and sewage feeding devices, and replicate model treatment plants designed to treat approximately 100 gallons of sewage per day. The waste supply, metal addition procedures, feeding schedules, analytical procedures, etc., (8, 13, 16, 17) are important factors, but time does not permit going into these essentials of effective investigation.

A diagram of the activated-sludge unit used is shown in Figure 2. Digestion has been studied in conventional digesters using primary sludge and excess secondary sludge produced by the primary and secondary treatment of the waste flow. The detention periods have varied from 16 to 26 days. A diagram of one of the digesters used is shown in Figure 19. The mixing apparatus was operated only once per day to thoroughly mix the sludge before withdrawing digester sludge, and after the feed of raw sludge. Sludges studied have consisted of primary sludge alone and mixtures made up of primary and secondary sludge containing 70 percent secondary sludge by volume.

An anaerobic digester is relatively slug-resistant. The contents are not part of the main stream of flow; a slug of waste can reach the digester only through sludge fed, and the daily feed is usually a small fraction of the digester contents. The digester is affected, however, by the concentration of metallic wastes in the part of the system where the main stream of flow occurs because the material removed therefrom is sent to the digester. In an operating plant most of the metallic wastes reaching a digester are metallic components of the sludges.

Concentration of metals in the waste treatment system occurs at two principal points. The first is in the primary sludge, where the maximum concentration would occur if all the metal were removed with this sludge. Here, the ratio of flow volume to primary sludge volume is a limiting factor. The secondary sludge is a second point where concentration can occur. Since the volume of secondary sludge removed from the system may be small compared to the flow through the system, concentration may be large at this point.

There is no net removal of metal if the primary and secondary sludges containing the metal are not removed permanently from the line of flow. For instance the extended aeration plant, common in Ohio, passes all the metal to the river unless secondary sludge is removed. If all the sludge is burned and the ash dumped in the river, there is little or no net removal of metal.

In an extended aeration system, sludge concentration of metal would be limited by losses of sludge, with the ratio of sludge concentration to influent metal concentration as the upper limit of the number of concentrations possible. Such a limit might be approached

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by an extended aeration plant that treats wastes of high metal content and does not waste sludge.

Figure 65 shows patterns of metal retention encountered. Curve 1 represents the type of retention curve shown by chromium introduced as chromate. Here, relatively inefficient reduction of hexavalent chromium in the system to more removable forms of chromium causes the behavior shown. Type 2 curves have been shown by most other metals. Curve 3 occurs where a limited amount of metal is removed by a mechanism with a limited capacity such as adsorption, coprecipitation, precipitation by a minor or inefficient precipitating agent, or some combination of such actions.

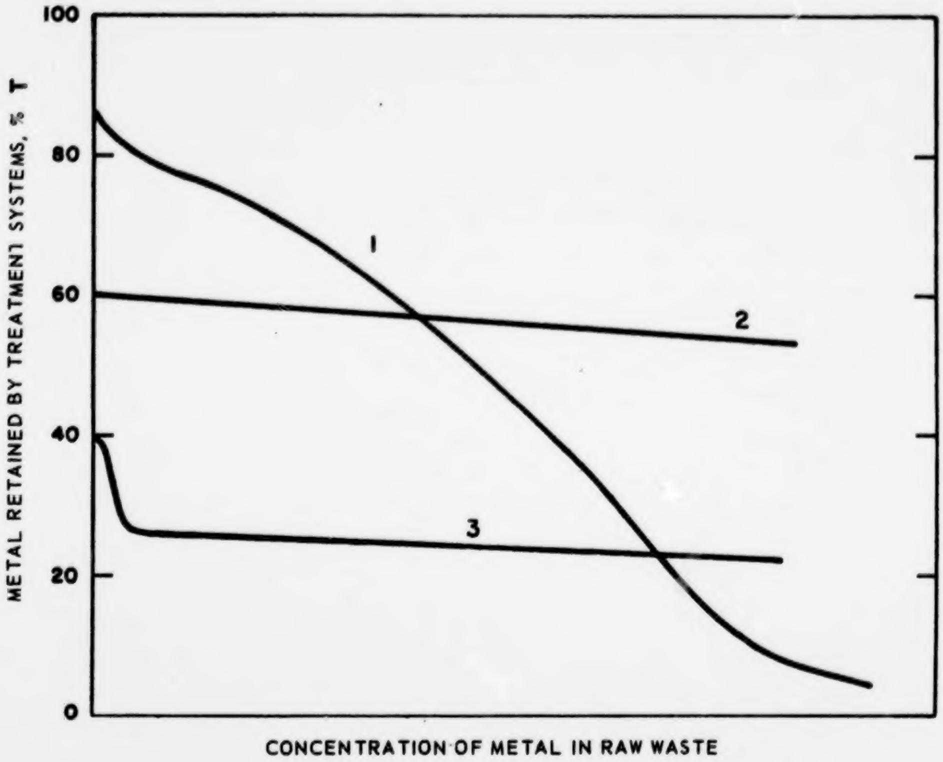

Figure 65. Patterns of heavy metal retention by treatment systems.

SEWAGE TREATMENT PROCESS REACTION TO METALS

Figure 66 shows general modes of reaction of sewage treatment processes to the continual presence of metals. In the aerobic part of the plant small amounts of metal make no detectable difference in the overall efficiency of treatment; larger amounts decrease treatment efficiency slightly. Over a very considerable range of metal increment, little increase in the organic content of the effluent occurs. While biological destruction or removal of organic matter is only slightly disturbed, the amount of oxygen used may be reduced because biological oxidation of nitrogen may be halted or minimized. Oxygen usage is obviously an observation of limited value in appraising organic treatment effectiveness where varying amounts of several kinds of sludge are withdrawn or where nitrification may vary.

As shown in Figure 66, in the anaerobic digester we have encountered only two sets of conditions: the digester performs adequately,

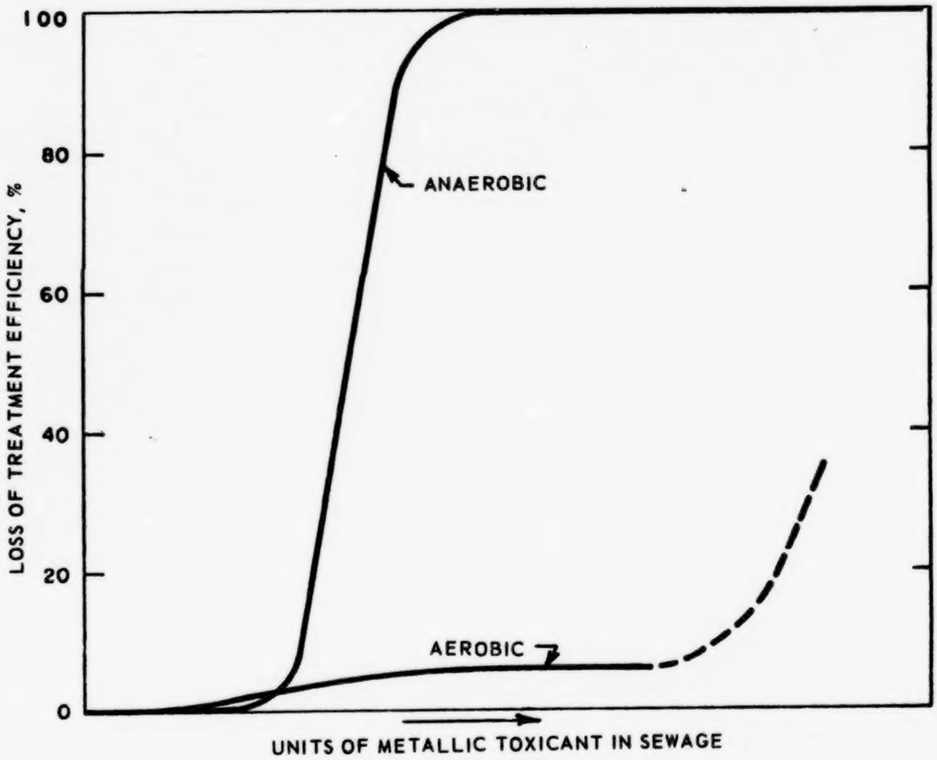

Figure 66. Patterns of performance depreciation in sewage treatment processes.

or the digester grinds to a halt and produces no gas. We have not observed any case in which the digester continues to function with reduced efficiency. As an additional observation, where digesters have contained dissolved sulfides, they have always worked; however, they have not always failed in the absence of sulfides.

Table 64 gives the tolerances of the complete activated-sludge process and anaerobic digestion to metals in the plant influent. Table 65 outlines some of the impairments of receiving waters related to the metal content of wastes. Where removal of organic matter is not critical, the most sensitive performance criterion may be the ability of the digester to handle the sludge. Since there are

Table 64. TOLERANCES OF SEWAGE TREATMENT PROCESSES TO METALS FED AT CONSTANT CONCENTRATION

Metal in raw sewage	Concentration in feed, ppm			
	Aerobic treatment		Anaerobic treatment	
	No observable effect on COD	Increases final effluent COD 20 ppm	Digestion of primary sludge	Digestion of primary + excess secondary sludge (3-7)
Copper	0.4	2.0	10	5
Chromium (as chromate)	>50	–	>50	>50
Nickel	1	>10	>40	10[a]
Zinc	10	>20	10	10

[a] Higher dose not studied.

alternatives to digestion, this need not be a bottleneck. In some situations metallic materials passing through the process may be highly objectionable. In our studies of chromate, we devised a means of biochemical reduction of this material to less objectionable and largely removed chromic chromium. This was done by modifying the activated-sludge process to force it to take oxygen from chromates (8).

Table 65. EFFECT OF METALS IN RAW SEWAGE ON SUITABILITY OF SECONDARY EFFLUENTS (CONVENTIONAL ACTIVATED SLUDGE) FOR DISCHARGE TO WATERS TO BE REUSED

Metal	Cosmetic factors	Dilution required to meet Drinking Water Std	Dilution required to protect fishes
Copper	Ugly turbidity above 2.5 ppm.	When Cu content of raw waste exceeds 1.3 ppm.	Tolerance of fishes estimated at 0.05 ppm. A high dilution may be required.
Chromium (as chromate)	Color at about 2 ppm in waste	High dilution required. Standard is 0.05 ppm.	Only with very high chromate (> 20 ppm.)
Zinc	Satisfactory at 2.5 ppm. Ugly turbidity at 10 ppm.	Satisfactory up to 10 ppm.	5 ppm is upper limit. Is reduced below 0.8 ppm by process.
Nickel	Ugly turbidity above 1.0 ppm	—	Waste exceeding 1.0 ppm requires dilution to be non-toxic to fishes.

In our examination of aerobic systems it has been necessary to base conclusions on replicate observations. The lower section of Figure 28 illustrates the effect of two forms of zinc on the overall performance of the sewage purification processes observed. Both sources of zinc caused a significant alteration of performance; and it is also clear that a small number of observations could not yield reliable data on the interplay of the metal and the system. The observations on complexed zinc were observations of systems previously acclimatized to cyanide so that it was destroyed in the course of aerobic treatment. Time is also required to enable the zinc content of the activated sludge to build up to a condition of operating equilibrium.

HARMFUL SLUG DOSE

Another of our objectives has been to define the amount of metal that, in a specific form, constitutes a harmful slug dose. What constitutes a harmful slug dose is determined by the waste volume, the volume and characteristic of the dilution water, and the usage of the stream below the point of waste entrance. As an example, we can, however, examine one facet of waste quality, the amount of organic matter penetrating waste treatment processes. Figure 28 also shows that the COD of the effluent from our plant exceeded 70 milligrams per liter only about 2 percent of the time. If we then take a COD average in excess of 70 milligrams per liter over a 24-hour period as a criterion of a harmful slug dose we arrive at the limits shown in Table 66. These conclusions are based on 4-hour slugs of metal fed to unacclimated sludges, and the worst 24 hours of subsequent performance.

Table 66. HARMFUL SLUG DOSES FOR UPPER 2 PERCENT OF CONTROL VALUES FOR 24 HOURS, AS MEASURED BY COD

Metal	Concentration (4-hour slug), ppm
Chromate	>500
Copper	75
Nickel	>50 <200

Such an evaluation should be based upon examination of performance disturbances caused by enough slug doses to give a suitable collection of reactions so that the behavior of large groups of slug doses could be compared to the range of behavior shown by normal substrates. Because these data cannot be procured without inordinate expense, we can only offer an insecure estimate of what constitutes an exceptional displacement of treatment plant performance as the result of a slug dose of metal.

CHAPTER VIII. ORGANIC LOAD AND TOXICITY OF COPPER TO ACTIVATED-SLUDGE PROCESS*

The Robert A. Taft Sanitary Engineering Center has studied the effects of heavy metals, singly and in combination, on the activated-sludge process. In these studies the organic load was approximately the same. The present investigation considers the effect of organic loading on the toxicity and the distribution of copper in the activated-sludge process. Copper was chosen because its toxicity is significant at a relatively low concentration and because preliminary work on the effect of organic loading had been reported previously (16).

PROCEDURE

The acitvated-sludge pilot plants used (Figure 2) were designed for complete treatment of sewage employing primary settling, aeration with continuous sludge return, and secondary settling. Sewage was fed at a constant rate. Sludge from the secondary settler was pumped continuously to the first chamber of the aerator at a rate of about 35 percent of the sewage flow. Sludge wasting rates were adjusted to hold mixed-liquor volatile-suspended-solids (MLVSS) concentrations between 1,000 and 1,200 milligrams per liter. Total detention time was 9 hours with a flow of 100 gallons per day.

The sewage used was domestic in origin and of relatively low strength because of ground-water infiltration. The sewage was fortified each day by addition of homogenized fish meal to the main holding tank. Average COD values of the sewage before and after additions were 200 and 380 milligrams per liter. The nutrient character of the fortified sewage was found to be adequate. The calculated BOD:N:P ratio was 100:6:3.

Three identical pilot plants were operated in parallel. One unit received undiluted fortified sewage at a constant rate. Copper sulfate solution was introduced at the sewage feed inlet continuously. The other two units were fed the same sewage diluted approximately 2:3 with tap water. Copper sulfate solution of the same concentration was introduced continuously in the influent sewage of one of these units; the other unit received no copper and served as a control. Since the MLVSS in the three units were maintained at approximately the same levels, the organic load on the units receiving diluted sewage was about one-half that of the unit receiving the strong sewage. The effects of two copper concentrations were studied at each organic load level. The concentrations selected were 1 and 5 milligrams per liter, present continuously in the influent sewage. The 5-milligram-per-liter copper run lasted about 6 months followed by the 1-milligram-per-liter copper run, which lasted about 2-1/2 months. The low-organic-load control was converted to a high-organic-load control during the last 2 weeks of the 5-milligram-per-liter copper run. The conversion was brought about by feeding this unit undiluted sewage. Experimental conditions with respect to units, load conditions, and copper runs are summarized in Table 67.

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*Paper presented at 19th Annual Purdue Industrial Waste Conference, Lafayette, Ind. See Reference 40.

Table 67. SUMMARIZED EXPERIMENTAL CONDITIONS

Pilot-plant type	Organic loading condition	Copper level and run
Control	Low	No copper
Control	High	
Copper fed	Low	1 mg/liter
	High	
	Low	5 mg/liter
	High	

COD, suspended solids, BOD, turbidity, and copper determinations of sampled outlets were used to measure the effects or organic loading and copper on the activated-sludge process.

SAMPLE COLLECTION AND ANALYTICAL METHODS

The sampling program for the study consisted of taking four 24-hour composites of feeds and primary and final effluents from the three units per week of operation. COD, suspended solids, and pH were determined on each of the 24-hour composites. BOD determinations were made twice a week. The samples were collected by means of an automatic sampler. The sewage flow was diverted for a few seconds every 15 minutes to gallon containers set in refrigerated chests. The 24-hour composites were homogenized by a blender, and analysis started within 3 hours after final collection. Daily turbidity determinations were made on grab samples of the final effluents from each unit. Mixed-liquor suspended solids and volatile suspendid solids were determined daily on grab samples taken from the aerator tanks.

Copper balances were calculated from total copper analysis of 7-day composites of sludges, feeds, and final effluents and grab samples from the aerators. Grab samples of mixed liquor were taken at the beginning and ending of each compositing period to determine the weekly accumulation of copper in the aerators.

Daily grab samples taken from primary and final effluent outlets were passed through an HA45 membrane filter and composited for 5 days. These samples were analyzed for soluble copper, which is arbitrarily defined as that portion of the total copper passing through the filter.

As has been our practice in previous metal toxicity studies, the units were acclimated to copper for 2 weeks prior to any sampling.

Analytical methods used are identical to those described in Chapter III, and generally follow *Standard Methods* (10) procedures. Exceptions were in the determination of COD, in which the mercuric sulfate modification (32) was used, and in the polarographic* determination of copper. By the latter, samples for either total- or soluble-copper analysis were wet-ashed with mixtures of nitric and sulfuric acids. Last traces of organic matter were destroyed by small additions of a mixture of perchloric and nitric acids. The dried residue was treated with an electrolyte solution, approximately 6 M in NH_4OH and 1 M in NH_4Cl. The solution was filtered through a sintered glass funnel, treated with small additions of powdered Na_2SO_3 to remove dissolved O_2, and then placed in the polarographic cell. The copper polarogram was recorded between 0.0 and -1.0 volts versus a saturated calomel electrode. The concentration of copper in the unknown was calculated from a determination of the height of the diffusion current trace at a half-wave potential of -0.45 volt against copper standards treated similarly. Tests run on several sewage samples with added amounts of copper gave 95 to 100 percent recoveries. The background concentration of copper in the raw sewage was less than 0.1 milligram per liter.

RESULTS AND DISCUSSION

Organic Loadings Obtained on Pilot-Plant Units

Daily organic loadings were calculated for high- and low-load units from determinations of COD of primary effluents and mixed-liquor volatile suspended solids of the aerators. The daily values were plotted as a frequency distribution on arithmetic probability paper. A straight-line plot indicates normal distribution of the data. The arithmetic mean point on the curve is directly above the 50 percent abscissa point, and the slope of the line is a measure of the standard deviation. The plots, means, and standard deviations are shown in Figure 67. By comparing the means, it can be seen that the organic load of the unit receiving the undiluted sewage was about twice that of the units receiving diluted sewage. The effect of dilution is shown by the smaller slopes of the lines of the low-loaded units. Daily organic loadings were not determined for the 1-milligram-per-liter runs because pilot plant operation was not changed, and the loadings shown on Figure 67 were not expected to change.

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*Sargent Model XV Polarograph.

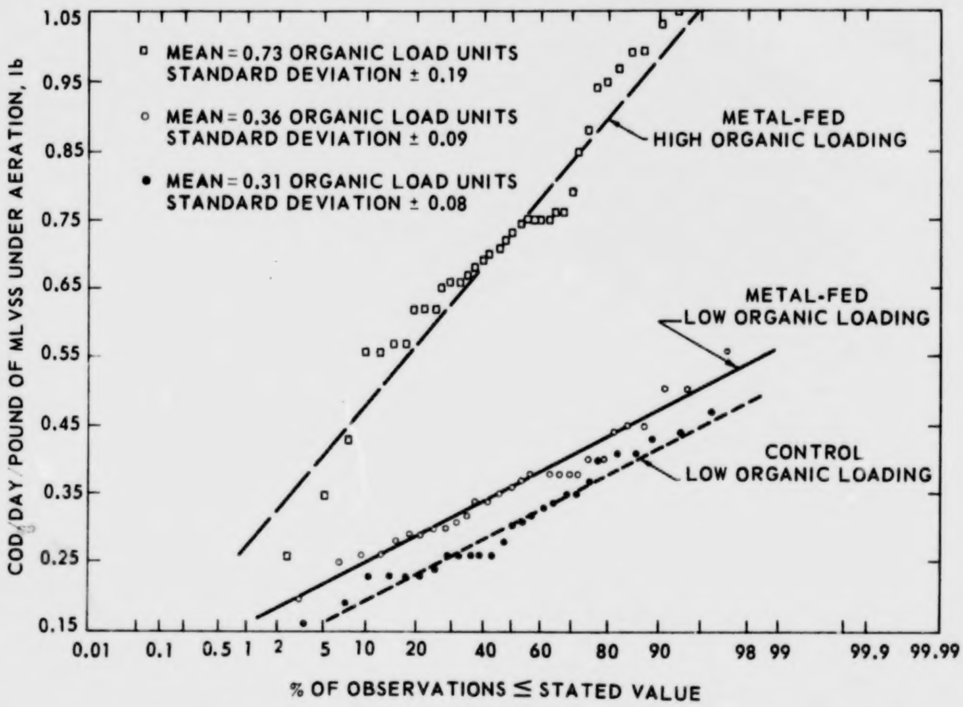

Figure 67. Daily variation of organic loading on activated-sludge pilot-plant units, 5-mg/liter copper run.

There is no standard way of expressing organic loading. For convenience, the organic loadings are expressed in various equivalent forms in Table 68.

Table 68. AVERAGE ORGANIC LOAD OF PILOT PLANTS

Pilot plant	Organic loading			
	COD units		BOD units	
	lb/day/ lb MLVSS under aeration	lb/day/ 1,000 ft^3 areation capacity	lb/day/ lb MLVSS under aeration	lb/day/ 1,000 ft^3 aeration capacity
Low organic load	0.31	22	0.14	10
Low organic load (5 mg Cu/liter)	0.36	24	0.16	11
High organic load (5 mg Cu/liter	0.73	57	0.32	25

Effects On Aerobic Treatment

The COD of the final effluents from the runs at 5 milligrams per liter copper are shown in Figure 68. The mean COD and standard deviation values were determined from the frequency distribution plots of the data. The curves for the two control units show that increasing the organic load increased the COD of the final effluent. Copper at 5 milligrams per liter had about the same effect on COD of the final effluent of the low-organic-load unit as doubling the organic load. Curves of the two metal-fed units show that effects of 5 milligrams per liter copper and organic loading on COD were roughly additive.

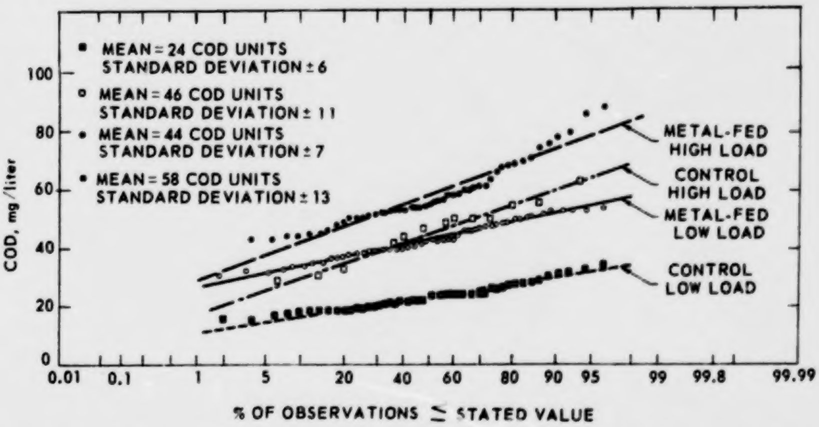

Figure 68. Statistical comparison of COD of final effluents in 5-mg/liter copper run.

Table 69 gives the characteristics of sewage feeds and primary and final effluents of each of the runs as arithmetic averages. Some of the data of Table 69 are shown graphically in Figures 69, 70, and 71 to make comparisons easier. Figure 69 shows that at the 1-milligram-per-liter concentration, the effect of copper was marginal at either load condition and that the increase in COD was almost entirely due to doubling the organic load. It was thought that, by choosing the run

Table 69. CHARACTERISTICS OF SEWAGE FEEDS, AND PRIMARY AND FINAL EFFLUENTS[a]

Load condition	Sampling outlet	COD, mg/liter	BOD, mg/liter	SS, mg/liter	Turbidity, stu	COD removal, feed to final effluent, %
Controls						
Low organic load	Feed	163	83	112	–	86
	Primary effluent	92	44	54	–	
	Final effluent	24	4	8	10	
High organic load	Feed	390	202	270	–	88
	Primary effluent	277	140	163	–	
	Final effluent	47	20	12	24	
1-mg/liter copper run						
Low organic load	Feed	226	115	161	–	88
	Primary effluent	126	63	92	–	
	Final effluent	27	5	9	9	
High organic load	Feed	418	195	273	–	88
	Primary effluent	242	137	136	–	
	Final effluent	50	11	9	16	
5-mg/liter copper run						
Low organic load	Feed	134	54	84	–	67
	Primary effluent	92	36	55	–	
	Final effluent	44	10	24	33	
High organic load	Feed	355	147	238	–	84
	Primary effluent	217	96	123	–	
	Final effluent	58	21	23	44	

[a] Arithmetic average.

with 1 milligram per liter copper, any enhancement of the toxicity as a result of the organic loading would be in sharp contrast to the previously determined marginal toxicity of copper at high organic

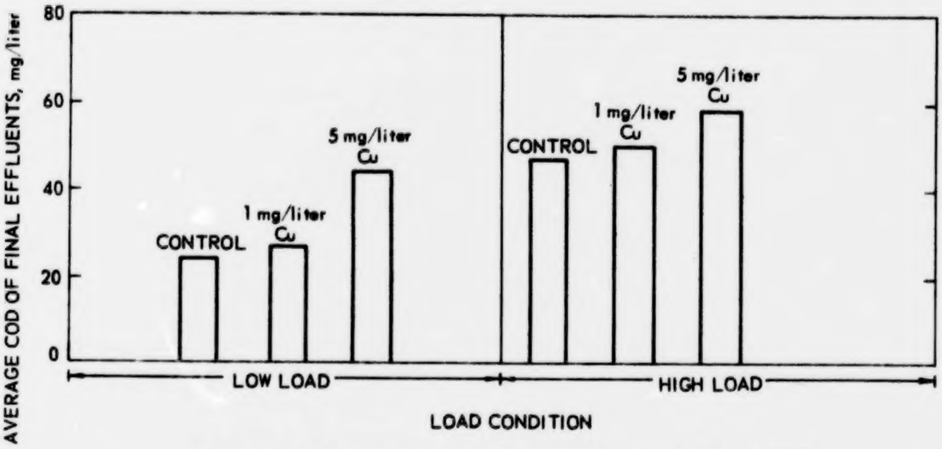

Figure 69. Comparison of effluent quality in terms of COD.

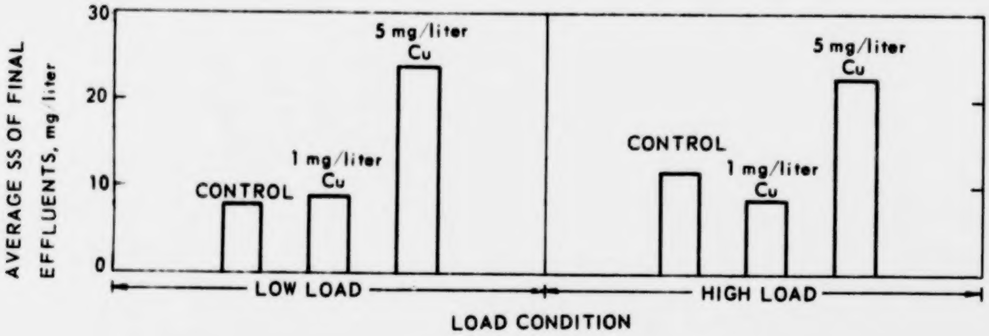

Figure 70. Comparison of effluent quality in terms of suspended solids.

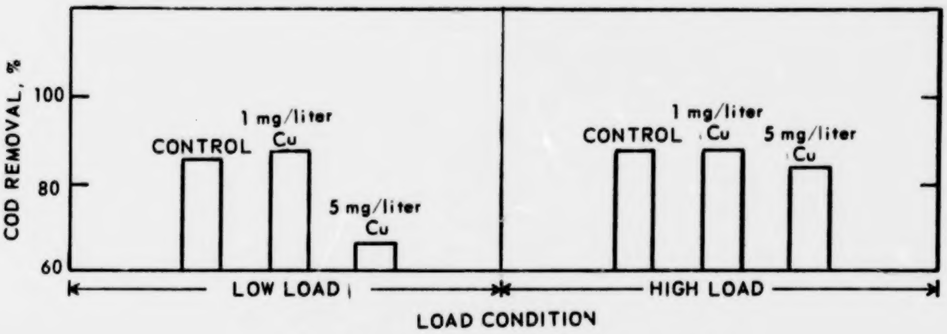

Figure 71. Comparison of aerobic efficiency.

load (16). This was not the case, and no differences in the effects of copper at 1 milligram per liter were noted under either load condition.

The data for the 5-milligram-per-liter copper runs in Figure 69 show that at the low-load condition COD in the final effluent increased more than the COD in the final effluent from the high-load metal-fed unit, compared with their respective controls. This should not be considered an indication of increased toxicity of copper at the low-organic-load condition and can be explained by reference to the solids data in Figure 70. These data show that the effluent of the low-loaded unit receiving 5 milligrams per liter copper contained a larger proportionate amount of suspended solids than any of the other effluents. This is probably related to the fact, as shown in Table 70 that the mixed liquor in this unit was high in ash content and, because of infrequent sludge wasting, was more typical of extended-aeration sludge, which produces a more turbid effluent than conventional activated sludge. The physical design of the final settler did not effectively remove this type of suspended matter from the effluent. The increased COD of this effluent is related to the increased solids present.

Table 70. AVERAGE CHARACTERISTICS OF MIXED LIQUOR IN 5-mg/liter COPPER RUN

Characteristic	Low organic loading control	Metal fed	
		Low organic loading	High organic loading
Suspended solids, % volatile matter	74	62	72
Sludge density index	2.0	2.1	1.4
Average concentration of copper, mg/liter	–	151	81

The data presented for the 1-milligram-per-liter copper runs at both load conditions in Figure 70 show that, at this copper concentration, no pronounced effect on the suspended solids of the effluents was found.

The most notable effect of the relation of organic load and metal toxicity is shown by the 5-milligram-per-liter copper run at low organic load in Figure 71 and Table 69. The percent COD removal was greatly reduced in this run, which by implication indicates an increase in metal toxicity; however, this is only an apparent increase. Direct comparison of the effluents from the two metal-fed units shows that the effluent from the unit removing only 67 percent of the influent COD was of better quality than that from the unit removing 84 percent. When a low-strength sewage, such as that used for the low-organic-load studies, is treated, any increment of extra material in the final effluent greatly influences the percent-overall-removal calculation.

Because of the variability of the data collected, as indicated by the standard deviations in Figures 67 and 68, it would be necessary to study a wider range of organic loads, aerator solids, and metal concentrations than those presented here, to establish firmly the entire relation of organic load and metal toxicity. These data, however, do show that moderate variation in organic loading does not markedly alter the effect of copper on the treatment process.

Fate Of Copper

The effects of organic loading on distribution of copper through process outlets during the runs with 5 milligrams per liter copper are shown in Tables 70 through 73. Table 71 shows that the total copper content in the two primaries was about the same. A small difference, which appears in the final effluents, indicated less total copper going out of the high-organic-load unit. The ratio of soluble copper to total copper shows that the high organic load produced a higher soluble-copper content in the primary and secondary effluents. This was probably due to the fact that the stronger sewage contained a larger concentration of complexing agents than the diluted sewage used to obtain the low organic loading did.

Table 71. AVERAGE CONCENTRATIONS AND FORMS OF COPPER IN PRIMARY AND FINAL EFFLUENT COMPOSITES IN 5-mg/liter COPPER RUN

Process outlet	Low organic loading	High organic loading
Primary effluent		
Soluble copper[a], mg/liter	1.2	1.8
Total copper[b], mg/liter	4.4	4.6
% $\frac{\text{soluble copper}}{\text{total copper}}$	27	39
Final effluent		
Soluble copper[a], mg/liter	0.5	0.7
Total copper[b], mg/liter	2.2	1.8
% $\frac{\text{soluble copper}}{\text{total copper}}$	23	39

[a] Soluble copper determined on the acid-digested filtrate.

[b] Total copper determined on the acid-digested unfiltered sample.

Copper balances were made at each load condition during the 5-milligram-per-liter copper run. Table 72 shows the average results obtained after combining 13 weekly balances for each metal-fed unit. The sludges removed from the high-organic-load unit contained more copper than those removed from the low-organic-

Table 72. AVERAGE COPPER BALANCES IN
5-mg/liter COPPER RUN

	Process outlet	Low organic loading	High organic loading
Copper fed found in outlets, %	Primary sludge	8	12
	Excess activated sludge	33	43
	Final effluent	50	39
	Unaccounted	-9	-6
Efficiency of copper removal, feed to final effluent, %		50	61

load unit, and, consequently, the efficiency of copper removal, expressed in percent, was greater in this unit. More copper was lost in the final effluent of the low-organic-load unit in association with the suspended solids of this effluent.

The average copper content of these sludges on a concentration basis is given in Table 73. The primary sludge from the low-organic-load unit had a copper concentration about one-half that of the high-organic-load unit on milligram-per-liter basis. On a milligram-per-gram total-solids basis, however, it contained more copper because there were less solids associated with primary sludge of the low-

Table 73. AVERAGE CONCENTRATIONS OF COPPER IN SLUDGES IN
5-mg/liter COPPER RUN

Process outlet	Low organic loading		High organic loading	
	mg/liter	Total dry solids, mg/g	mg/liter	Total dry solids, mg/g
Primary sludge	71	11	116	5.5
Excess activated sludge	388	77	180	36

organic-load unit. The excess activated sludge produced by the low-organic-load unit contained considerably more copper than that of the other unit. This condition was brought about by infrequent sludge wasting, which caused a buildup of copper in the aeration solids. At the higher load condition, frequent sludge wasting was necessary to maintain a constant aerator solids level, and, consequently, copper did not build up to the same extent.

The characteristics of the mixed liquor during the 5-milligram-per-liter copper runs are given in Table 70. As a result of the greater ash content of the sludge, the percent MLVSS value of the low-organic-load unit was lower and the sludge density index value was higher than the corresponding values of the high-organic-load unit.

SUMMARY

Moderate variations of organic loading did not markedly affect the toxicity of copper to the activated-sludge process, under the conditions employed in this study.

Increasing the organic load increases the COD of the effluent.

The effect of 5 milligrams per liter copper fed continuously to a low-organic-loaded unit had about the same effect on COD of the effluent as doubling the organic load. The suspended solids in the final effluent of this unit were more than would be expected from conventional activated-sludge treatment.

Organic loading altered the distribution and form of metal during the 5-milligram-per-liter copper studies. The unit receiving the high organic load was more efficient in removal of copper and produced a higher ratio of soluble to total copper in the process effluents.

In order to observe effects due to copper toxicity alone, reasonable control of organic loading and aerator solids is necessary, and a parallel control unit is recommended.

GPO 820-663-11

CHAPTER IX. A SLUG OF CHROMIC ACID PASSES THROUGH A MUNICIPAL TREATMENT PLANT*

Previous studies conducted at the Robert A. Taft Sanitary Engineering Center using pilot-scale, activated-sludge sewage treatment plants indicated that a 10-milligram-per-liter slug of chromium lasting 4 hours had no effect whatsoever on plant performance, while 100- and 500-milligram-per-liter slugs caused the plant efficiency, as measured by BOD removal, to drop by 3 and 10 percent, respectively, during the first 24 hours (8).

A field study was undertaken to complement the pilot-scale study. The objective was to determine the effects of passage of a prearranged slug of chromic acid on the efficiency of the Bryan, Ohio, municipal sewage treatment plant. This chapter presents the results of this study. In addition to the levels of chromium in the plant processes attributable to the chromic acid slug, background data on the concentrations of chromium, copper, zinc, and nickel are presented also.

CONDUCT OF STUDY

Plant Description

The Bryan, Ohio, sewage treatment plant serves a community of 7,400 persons with an equivalent population of 12,000. The plant has conventional activated-sludge secondary treatment, an average sewage flow of 0.8 mgd, and a design flow of 1.9 mgd. A flow chart for the plant is shown in Figure 72.

The sewage, after passing through the grit chamber and comminutors, enters a wet well from which it is pumped into the primary clarifiers. The effluent from the four primary clarifiers passes through the first of the three aeration tanks. The mixed liquor from this tank is divided equally between the remaining two tanks, from which it flows into the final clarifiers. The effluent from the clarifiers is discharged to drainage ditch number 40 and comprises 90 percent of the flow. The ditch discharges into Lick Creek, a tributary of the Tiffin River, 11-1/2 miles below the plant outfall sewer.

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*Paper presented at 19th Annual Purdue Industrial Waste Conference. Lafayette, Ind. See Reference 35.

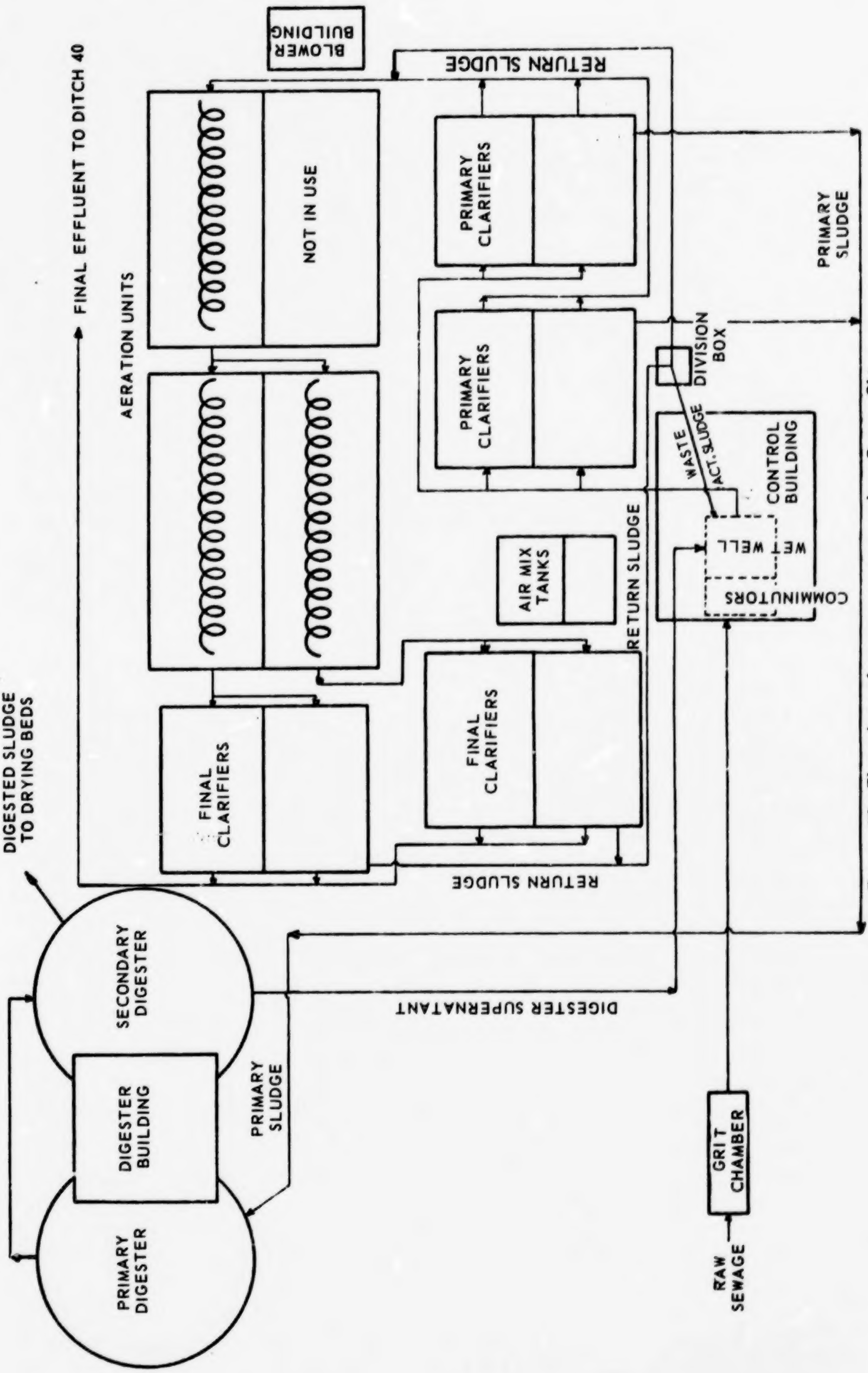
FINAL EFFLUENT TO DITCH 40
BLOWER BUILDING
RETURN SLUDGE
AERATION UNITS
NOT IN USE
PRIMARY CLARIFIERS
PRIMARY CLARIFIERS
PRIMARY SLUDGE
DIVISION BOX
WASTE ACT. SLUDGE
CONTROL BUILDING
WET WELL
COMMINUTORS
AIR MIX TANKS
RETURN SLUDGE
DIGESTED SLUDGE TO DRYING BEDS
FINAL CLARIFIERS
FINAL CLARIFIERS
RETURN SLUDGE
SECONDARY DIGESTER
DIGESTER SUPERNATANT
DIGESTER BUILDING
PRIMARY SLUDGE
PRIMARY DIGESTER
GRIT CHAMBER
RAW SEWAGE

Figure 72. Flow chart of sewage treatment plant Bryan, Ohio.

Ninety-two percent of the sludge pumped from the final clarifiers is returned to the first aeration unit, and the remaining 8 percent is wasted to the raw sewage in the wet well. The return sludge flow averages 87 percent of the raw sewage flow at Bryan.

The sludge in the primary clarifiers is pumped to the primary digester twice each day from 8 to 9 in the morning and 3 to 4 in the afternoon. Supernatant is withdrawn from the secondary digester and returned to the sewage wet well. Digested sludge is pumped to sand drying beds and ultimately disposed of in fill areas. Design data and loading factors for the various plant processes previously mentioned are presented in Table 74.

Table 74. PLANT DATA AND LOADING FACTORS

Process	Design data and loading factors	
Primary clarifier	Capacity	4 @ 4,440 ft^3 ea = 17,800 ft^3
	Detention at 0.8 mgd	4 hr
	Surface overflow rate	390 gpd/ft^2
	Weir overflow rate	13,800 gal/ft of weir/day
Aeration unit	Capacity	2 @ 23,300 ft^3 1 @ 18,000 ft^3 } 64,600 ft^3
	Detention at 0.8 mgd	14 hr
	Loading	
	BOD	0.5 lb/day/lb VSS 22 lb/day/1,000 ft^3
	COD	1.0 lb/day/lb VSS 47 lb/day/1,000 ft^3
	MLVSS	720 mg/liter
	Air supplied	2.4 ft^3/gal of sewage
Final	Capacity	4 @ 5,840 ft^3 ea = 23,300 ft^3
	Detention at 0.8 mgd	5 hr
	Surface overflow rate	390 gpd/ft^2
	Weir overflow rate	2,700 gal/ft of weir/day
Anaerobic digestion	Capacity	Primary – 45,700 ft^3 Secondary – 33,200 ft^3
	Detention time	10 days
	Loading	100 lb VS/day/1,000 ft^3

Arrangements For Slug

The industries in Bryan, Ohio, discharging metallic wastes into the municipal sewers include the ARO Corporation and a small-scale job plater. The ARO Corporation designs and manufactures pneumatic tools, industrial pumping units, lubricating equipment, and aircraft products and has a metal-plating department that plates the various components. The job plater handles orders from local industries and organizations that have materials to be plated, but do not have plating equipment.

With the cooperation of the officials of the city of Bryan, the ARO Corporation, and the Department of Health of the State of Ohio, arrangements were made to dump 150 gallons of chromic acid anodizing solution into the municipal sewers, where it would ultimately enter the sewage treatment plant.

The ARO Corporation furnished chromic acid solution that had been used to anodize aluminum parts by the electrochemical conversion of their surfaces to aluminum oxide, which increased their corrosion protection. The chromic acid in the anodizing bath is inactivated by neutralization because the alumina dissolves as the anodic film forms. The procedure used at ARO to renew a bath is to withdraw a portion of the bath periodically and replace it with fresh chromic acid. Of one of these portions, 150 gallons was saved. The chromic acid solution had a pH of 0.8, and the 150 gallons contained 50 pounds of hexavalent chromium. The personnel at ARO dumped the solution into their sewer in 9 minutes, beginning at 8:00 a.m., December 4, 1963.

Sampling Procedures

An around-the-clock 5-day sampling program, to determine the concentration and distribution of heavy metals in the aerobic and anaerobic treatment processes, before and after the chromic acid entered the plant, was carried out with specific emphasis on chromium.

Grab samples of the sewage were taken every 5 minutes during the height of the slug. Grab samples of the primary clarifier effluent and mixed liquor were taken at various time intervals to establish the variation of chromium in these steps of the process. Daily composites of raw sewage, primary clarifier effluent, final clarifier effluent, and return sludge were made up of hourly grab samples. All sampling was done by hand, and where applicable, proportioned to flow.

Analytical Methods

Chromium was determined by using the permanganate-azide method outlined in *Standard Methods* (10). A polarographic procedure was used to analyze samples for copper, zinc, and nickel. The samples for metal analyses were evaporated and digested with acid to remove the organic matter according to the procedure outlined in *Standard Methods*. The other methods used in this study also conform to those given in *Standard Methods*. Soluble metals are defined as those passing through an HA45 membrane filter.

RESULTS

Chromic Acid Slug

The slug of chromic acid began arriving at the plant at 10:43 a.m., 2 hours and 40 minutes after it was dumped at the ARO Corporation. It lasted for 1 hour in the incoming sewage. The concentrations of chromium in the raw sewage and the primary clarifier effluent during the slug and several hours thereafter are presented in Figure 73. The pH values of the sewage and primary effluent during the slug are also included.

The sewage had a chromium concentration of 500 milligrams per liter and a pH value of 5.7 during the height of the slug. Traces of chromium were noted in the effluent at the weir of one of the four primary clarifiers 15 minutes after the peak concentration occurred in the sewage. The peak concentration of chromium in the primary clarifier effluent was 65 milligrams per liter with a corresponding pH value of 6.8. Eighty percent of the chromium in both the sewage and primary effluent was in solution.

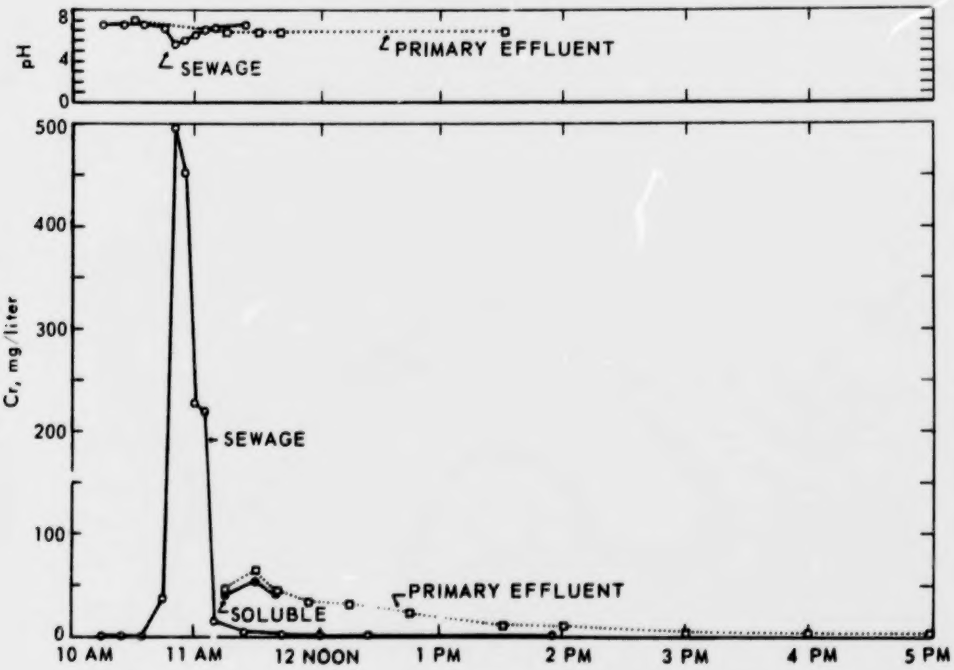

Figure 73. Concentration of Chromium in sewage and primary effluent.

The variation in concentration of chromium in the primary sludge on the basis of milligram per liter and milligram per gram of total solids (TS), the variation in quantity of chromium, and the variation in the volume of primary sludge during the study are all illustrated in Figure 74. The quantity of chromium in the sludge pumped to the digester after the slug was similar to that pumped routinely before the slug.

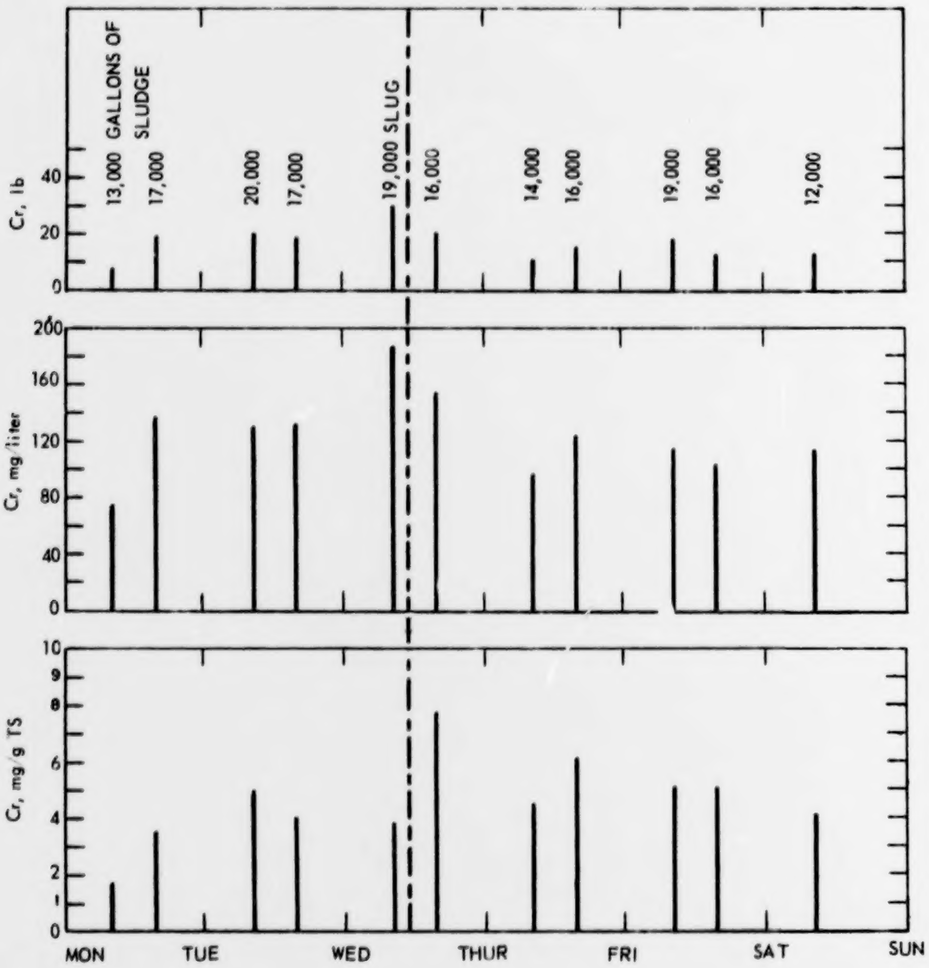

Figure 74. Chromium in primary clarifier sludge.

Presented in Figure 75 are the concentrations of chromium and suspended solids in mixed-liquor samples taken before and after the slug entered the plant. The chromium increased from an average of 3 milligrams per liter just prior to the slug to 13 milligrams per liter 3 hours after and remained at an average concentration of 10 milligrams per liter during the remainder of the study. The concentration of chromium on a basis of milligrams per gram of total solids in the return sludge is shown in Figure 76. The chromium is significantly higher after the slug.

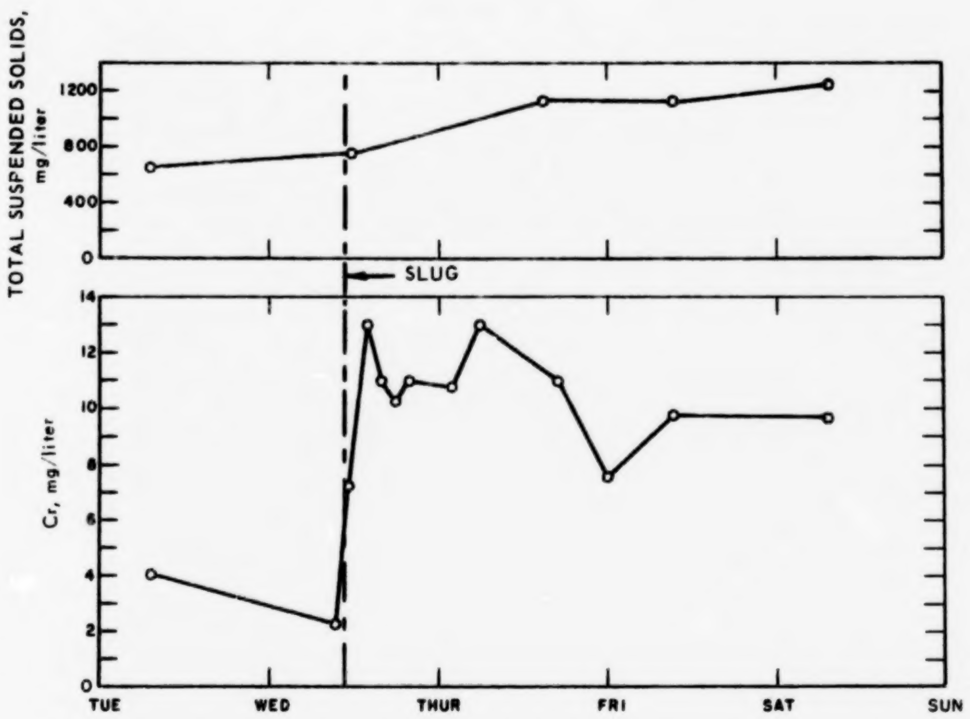

Figure 75. Chromium in aeration unit.

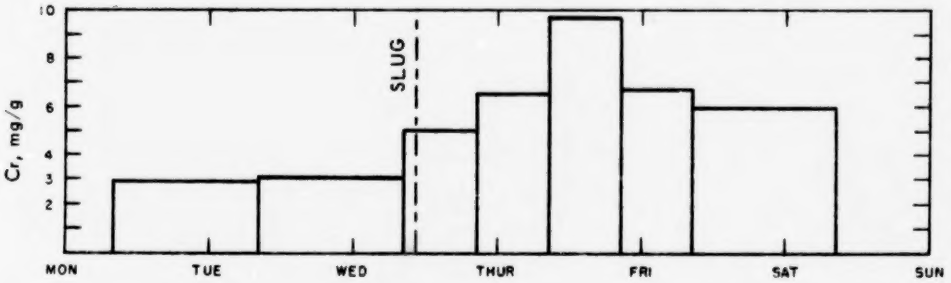

Figure 76. Chromium in return sludge.

The variation in the concentration and quantity of chromium in the final effluent is presented in Figure 77. Ninety percent of the chromium leaving the plant in the 1-day period following the slug was in a soluble form. Chromium was detected in Lick Creek in a concentration of 0.3 milligram per liter approximately 22 hours after the slug entered the plant. The concentration before the slug was less than 0.1 milligram per liter.

The concentration of chromium in the primary digester and the variation in the daily gas production are illustrated in Figure 78. The cubic feet of gas produced per pound of volatile solids fed to the digesters for the 3-day period following the slug is also included

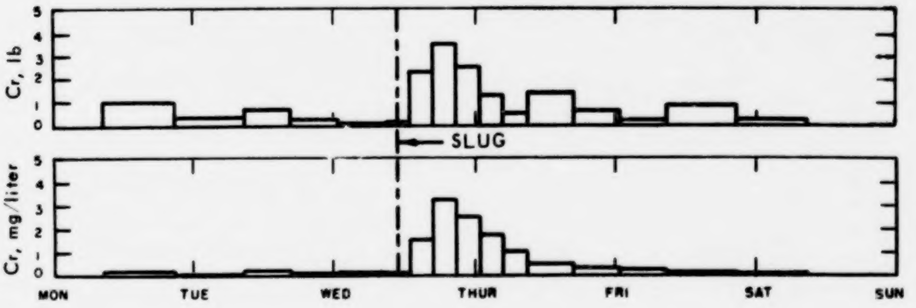

Figure 77. Chromium in final clarifier effluent.

in Figure 78. The digester contents had the following characteristics; pH, 6.8; volatile acids, 800 milligrams per liter; alkalinity ($CaCO_3$), 1,800 milligrams per liter; temperature, 77° F.

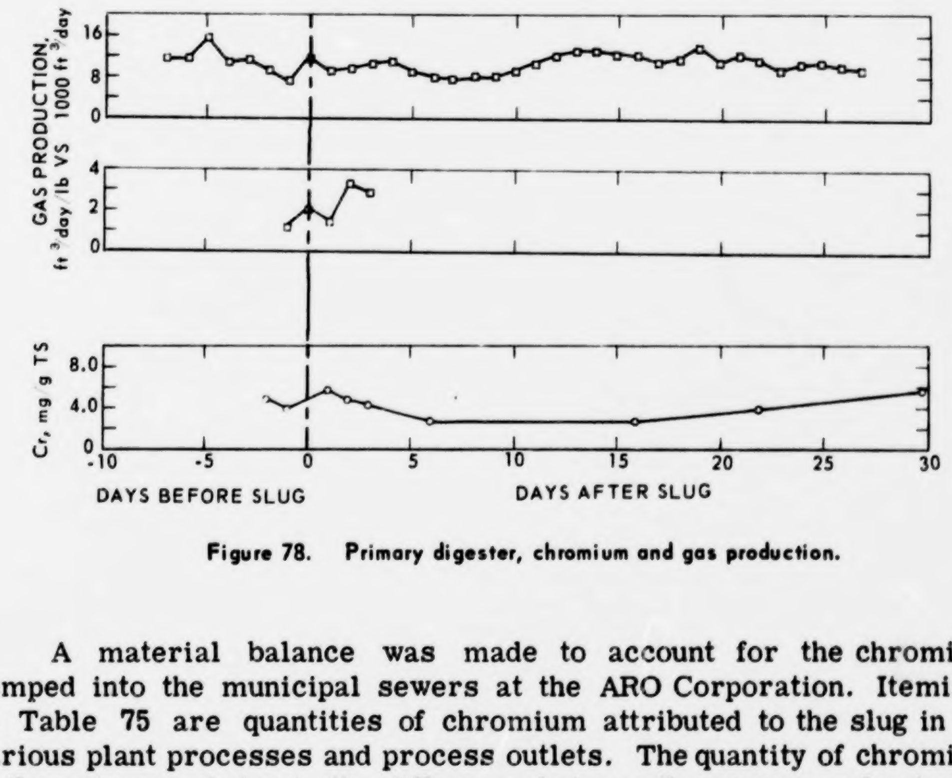

Figure 78. Primary digester, chromium and gas production.

A material balance was made to account for the chromium dumped into the municipal sewers at the ARO Corporation. Itemized in Table 75 are quantities of chromium attributed to the slug in the various plant processes and process outlets. The quantity of chromium in the primary sludge is the difference between the sewage and primary clarifier effluent quantities.

The quantity of chromium entering the plant in the sewage was calculated by plotting the concentration of chromium during the slug versus the volume of sewage and determining the area enclosed by this curve. This calculated quantity (43 pounds) and the 50 pounds dumped at ARO were averaged to give the value in Table 75. The quantity of chromium in the primary effluent was determined by

Table 75. DISTRIBUTION OF CHROMIUM IN THE PLANT

Source	Chromium, lb
Sewage	47
Primary effluent	37
Primary sludge (by difference)	10
Aeration tanks	25
Waste sludge	4
Final effluent	10

using concentration and flow data. The quantities of chromium in the aeration tank, final effluent, and waste sludge were determined by subtracting quantities of chromium in a 1-day period prior to the slug from the 1-day period immediately after.

Since the waste sludge is returned to the primary clarifier, a portion of the 4 pounds of chromium from the slug leaves via the primary sludge while the remainder enters the aeration chamber via the primary clarifier effluent, and some of the 4 pounds of chromium in the waste sludge is, therefore, included in the quantity of the aeration tank. The sum of the quantities of the chromium in the aeration chamber, the final effluent, and waste sludge is similar to that calculated in the primary effluent.

COD, BOD, SS, and turbidity data for 12-, 8-, and 4-hour composite samples of final effluent taken before and after the slug entered the plant are presented in Figure 79.

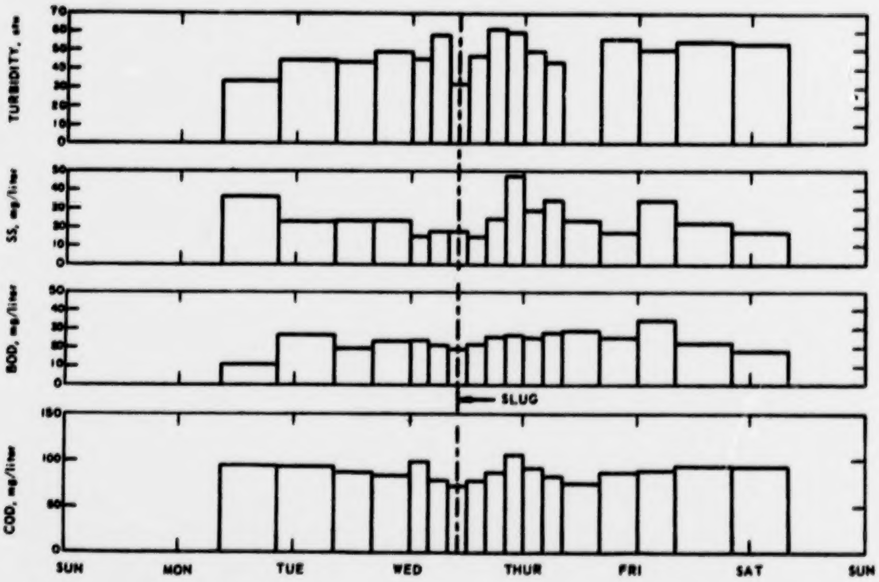

Figure 79. COD, BOD, Suspended solids, and turbidity in final clarifier effluent.

Background Metals

Illustrated in Figure 80 are the daily average concentrations of metals and cyanide in the sewage (solid lines) and primary clarifier effluent (dashed lines). The significant increase in the chromium concentration of the 24-hour composite beginning Wednesday was due to the chromium slug. A slug of copper entered the plant on Friday, but was not detected until later analysis of samples. It is evident from Figure 80 that the copper slug was associated with cyanide in a copper cyanide complex, since a significantly higher concentration of cyanide was also detected in the Friday sewage composite than in previous composite samples. The concentration of chromium in the 24-hour sewage composite on the day of the slug was less than that in the primary effluent sample for the same period. In the case of the copper slug, the sewage composite had a higher concentration than the primary effluent had.

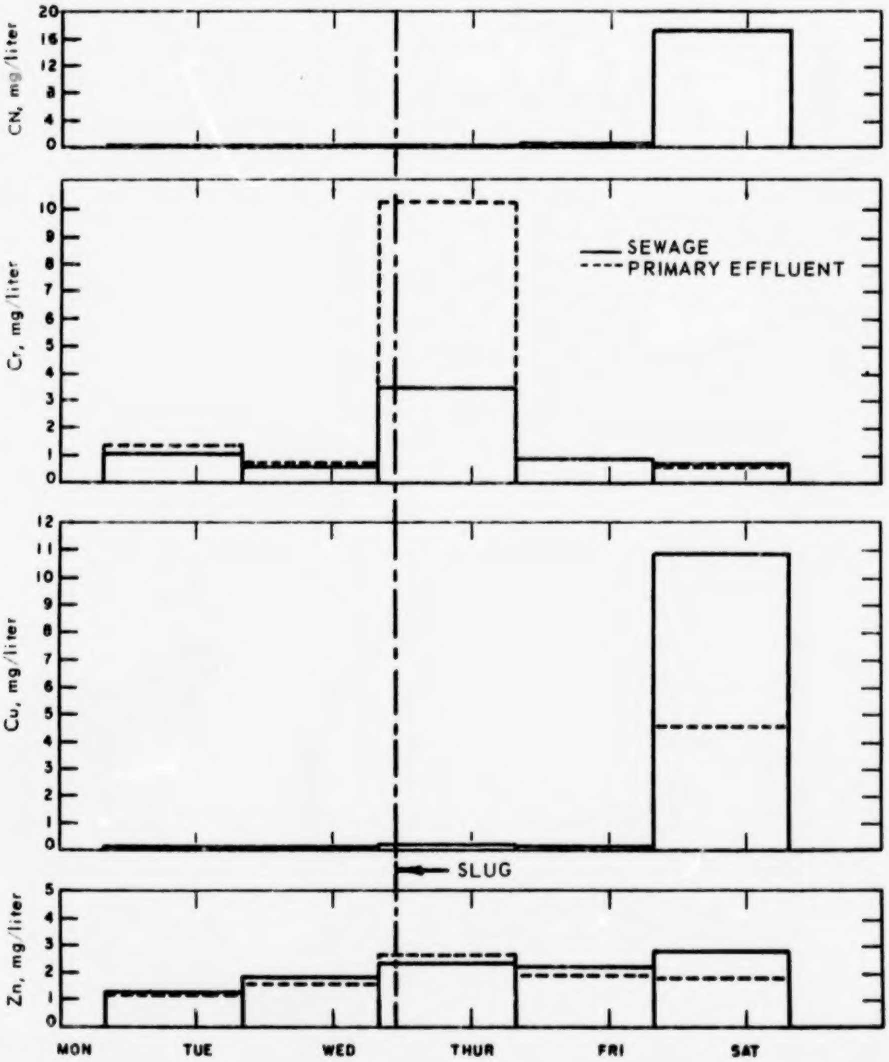

Figure 80. Background metals in sewage and primary effluent.

Table 76. METALS IN SEWAGE AND PROCESS EFFLUENTS

		Concentration in 24-hour composites, mg/liter								
Source	Metal type	Chromium		Copper		Zinc		Nickel		Total of 4 metals
		Avg	Range	Avg	Range	Avg	Range	Avg	Range	
Sewage	Total	0.8	0.6–1.1	0.2	0.17–0.25	2.2	1.4–2.9	0.05	0.03–0.07	3.3
Primary effluent	Total	0.9	0.6–1.5	0.2	0.1 –0.3	1.8	1.2–2.7	0.06	0.05–0.09	3.0
	Soluble	0.5	0.1–1.2	0.09	Trace–0.2	0.3	0.1–0.5	0.06	0.03–0.10	1.0
Final effluent	Total	0.2	0.2–0.3	0.1	0.04–0.1	0.2	0.17–0.29	0.05	0.03–0.07	0.5
	Soluble	0.2	0.1–0.4	0.1	0.05–0.2	0.2	0.11–0.30	0.05	0.04–0.14	0.5
Concentrations in primary clarifier influent attributed to digester supernatant and waste sludge, mg/liter										
Digester supernatant	Total	2.6	–	0.1	–	2.7	–	0.06	–	5.5
Waste-activated sludge	Total	1.2	–	0.2	–	1.5	–	0.01	–	2.9

A summary of the averages and ranges of concentrations of metals in the sewage, and the primary and final clarifier effluents for the 5-day study is presented in Table 76. The 24-hour composite samples reflecting increases in metal concentrations due to the slugs of chromium and copper are not included in the table. Zinc was present in larger average continuous concentrations in the sewage than any other metals. Zinc averaged 2.2 milligrams per liter while chromium, copper, and nickel, with slug concentrations omitted, averaged 0.8, 0.2, and 0.05 milligram per liter, respectively.

Since the digester supernatant and waste-activated sludge are returned to the sewage prior to its entering the primary clarifiers, the concentrations of metals in the primary clarifier influent contributed by these sources are also included in Table 76. The data were obtained by dividing the quantity of each returned to the sewage during the 5-day study by the total volume of sewage during the same period. The concentrations of chromium and zinc attributed to supernatant and waste sludge are greater than those in the sewage. The data in Table 76 indicate that approximately 100 percent of the metals in the final effluent were soluble as compared with 35 percent in the primary effluent.

Presented in Table 77 are the concentrations of metals in the mixed liquor, and primary and return sludges. The average concentrations of metals in the primary digester and digester supernatant are shown in Table 78. These tables are based on the average of 5 days of analyses.

Table 77. METALS IN MIXED LIQUOR, AND PRIMARY AND RETURN SLUDGES

Sludges	Units	Total metals			
		Chromium	Copper	Zinc	Nickel
Primary	mg/liter	125	36.1	242	1.7
	mg/g total solids	4.7	1.3	11.7	0.05
Return	mg/liter	17.2	2.2	20.4	0.1
	mg/g total solids	5.3	0.7	6.3	0.04
Mixed liquor	mg/liter	9.3	1.2	9.9	0.07

Table 78. METALS IN DIGESTER AND DIGESTER SUPERNATANT

Source	Units	Total metals			
		Chromium	Copper	Zinc	Nickel
Digester	mg/liter	88	27	220	2
	mg/g total solids	4.3	1.3	10.6	0.1
Digester supernatant	mg/liter	77	4.0	82	1.9
		Soluble metals			
Digester	mg/liter	0.09	0.13	0.16	0.05

The BOD, COD, and suspended solids data for 24-hour composite samples of raw sewage, primary clarifier effluent, and final clarifier effluent collected during the study are presented in Table 79. The sewage contained 24 milligrams per liter of total nitrogen and the primary effluent 38 milligrams per liter. The higher nitrogen in the primary effluent is caused by recycling digester supernatant. No nitrate nitrogen was present in the final effluent, either before or after the chromic acid slug. Ammonia nitrogen was present in the final effluent in a concentration of 19 milligrams per liter during the study. The dissolved oxygen levels in the first aerator and the final clarifiers were 0.4 and 1.1 milligrams per liter, respectively.

Table 79. SEWAGE AND PROCESS EFFLUENT CHARACTERISTICS

	Raw sewage,		Primary clarifier effluent			Final clarifier effluent		
Analysis	Avg, mg/liter	Range, mg/liter	Avg, mg/liter	Range, mg/liter	Removed, %	Avg, mg/liter	Range, mg/liter	Removed, %
BOD	325	275-359	216	182-256	33	25	20–30	92
COD	603	481-754	451	391-517	24	90	85–96	85
Suspended solids	164	100-216	141	98–166	13	25	21–30	84

DISCUSSION

A controlled slug of chromic acid entered the treatment plant and lasted for 1 hour in the sewage, with 95 percent of the chromium entering the primary clarifier in 25 minutes. The chromium slug short-circuited along the bottom of one of the primary clarifiers and appeared in the primary effluent before any trace of the characteristic greenish-yellow color was noted in the clarifier itself. Owing to detention in the clarifiers, chromium from the slug appeared in the effluent up to 12 hours after the slug entered.

Thirty-seven pounds of chromium was accounted for in the primary effluent. With a value of 47 pounds, which is an average of the quantity of chromium dumped at the ARO Corporation and that calculated in the sewage at the plant, 10 pounds had to be accounted for in the primary sludge. Since the background quantity of chromium was unknown for the primary sludge removed at 3:00 p.m., the day of the slug, this value arrived at by difference could not be confirmed.

The 37 pounds of chromium leaving the primary clarifiers is reasonably accounted for in the aeration units, final effluent, and waste sludge, as is shown in Table 75. If the figures of 47 pounds of chromium entering the plant and 10 pounds leaving via the final effluent 1 day after the slug are used as a basis, then approximately 80 percent was retained by the plant processes.

Since the return sludge rate is significantly greater than that of the typical average activated-sludge plant, more metal is recirculated back to the aeration chambers to be detained and dribbled out in small quantities via the final effluent. This is evident from the chromium concentration in the mixed liquor shown in Figure 76. Three days after the slug entered the plant, the concentration was 10 milligrams per liter in the aeration chambers, which is only 3 milligrams per liter less than the peak value several hours after the slug.

The reason for the significant increase in the concentration of chromium in the digester contents after the slug is obscure (Figure 78), since the 10 pounds in the primary sludge attributed to the slug was only 5 percent of the quantity of chromium in the digester prior to the slug. The quantity of chromium pumped to the digester after the slug was similar to that pumped before the slug. Gas production was not adversely affected. An anaerobic digester is not on the main flow stream, and coupled with its large retention volume, it is greatly less subject to shock than is commonly thought.

In view of the precision of the parameters used to evaluate effluent quality, and the normal variation from hour to hour and day to day that can be expected when dealing with a municipal treatment plant, there was no significant difference in overall effluent quality attributable to the slug of chromic acid.

The difference between the 24-hour composite concentrations of chromium in the sewage and primary effluent was due to the method of sampling. The 24-hour composite samples were made up of 24 hourly grabs taken on the hour. A sample of raw sewage was taken while the slug was in progress, since 95 percent of the chromium entered the plant in 25 minutes and the entire slug lasted only 1 hour, and this was the only grab sample of the sewage containing chromium from the slug. In the case of the primary effluent, in which the slug lasted about 12 hours, 12 samples that contained chromium were taken from the slug. This would account for the higher 24-hour concentration in the primary effluent.

The same reasoning applies to the copper slug, except that the sewage sample must have been taken near the time the peak concentration occurred in the sewage, which introduced more copper into the sewage composite in one grab sample than several grabs of primary effluent did for its 24-hour composite.

If both slugs had occurred shortly after the hour and ended shortly before, the 24-hour raw sewage samples would not have indicated the presence of the slugs.

If the unannounced slug of copper and cyanide entering the plant on the last day of the study had occurred sooner, and a significant effect on plant efficiency had taken place, an effect attributable to chromium would have been difficult to determine. This incident illustrates one of the differences in pilot-scale and full-scale studies. In pilot-scale work, full control can be exercised over the influent to the plant, but a municipal plant operator has no such control.

The slug of copper cyanide was not detected during the sampling program by the project personnel since there was no visible indication of its presence as is the case with chromium, which is readily identified by its greenish-yellow color. No data are available on the effect of the copper cyanide slug on the quality of the plant effluent. In view of the gas production shown in Figure 78, however, the digester was not significantly affected by the copper slug.

The sum of the background metals in the sewage, when the chromium and copper slug data are omitted, was approximately 3 milligrams per liter, with zinc responsible for two-thirds of this concentration.

Since the Bryan plant receives less than one-half of its design flow, the detention times in the processes are longer than those in the average plant. The return sludge rate is also higher at Bryan, averaging between 80 to 90 percent of the sewage flow. The percent removal of chromium in a plant with a shorter detention period and a 20 percent return sludge rate may not be so high, and, consequently, higher concentrations of chromium in the receiving water would be expected.

Even though this study has demonstrated that the biological processes employed by municipal sewage plants are reasonably tolerant to slugs of chromium, it is not recommended that chromium wastes be indiscriminately dumped into the sewers. With the increasing reuse of surface water, the metal content of a plant effluent becomes important.

SUMMARY

A field study to determine the effects of a controlled slug of chromic acid on the efficiency of the Bryan, Ohio, municipal sewage treatment plant was undertaken. The slug contained 47 pounds of chromium, and concentrations reached 500 milligrams per liter in the sewage. Ninety-five percent of the chromium entered in a 25-minute period and the entire slug lasted 1 hour. Approximately 80 percent of the chromium in the slug was retained by the plant processes, and no significant adverse effects on these processes, both aerobic and anaerobic, were noted.

GPO 820—663—12

CHAPTER X. FOUR MUNICIPAL TREATMENT PLANTS RECEIVING METALLIC WASTES*

Four municipal sewage treatment plants were selected for a field survey concerning the receipt of copper, chromium, nickel, and zinc; distribution of the metals in the plant processes; and effects of the metals on the biological phases of treatment.

The plants were chosen on the bases of a history of receiving metallic wastes, good management by cooperative officials, and proximity to the Robert A. Taft Sanitary Engineering Center.

Activated-sludge plants in Bryan, Ohio; Grand Rapids, Michigan; and Richmond, Indiana, and a high-rate trickling filter plant in Rockford, Illinois, were each visited by a field crew for a 2-week period. A brief synopsis of the plants is shown in Table 80. The design and loading factors for each plant can be found in Tables 74, 81, 82, and 83.

Table 80. MUNICIPAL SEWAGE TREATMENT PLANTS

Location	Population served	Average daily flow, mgd	Design flow, mgd	Average sewage BOD, mg/liter	Type of treatment
Bryan, Ohio	7,400	0.8	1,9	325	Activated sludge
Richmond, Indiana	46,000	6.8	18.0	113	Activated sludge
Rockford, Illinois	175,000	28.5	(Including recycle) 45.0	128	High-rate trickling filter
Grand Rapids, Michigan	225,000	35.0	44.0	96	Activated sludge

The objective of this study was to find whether field observations would substantiate earlier pilot-scale studies and enable this large reservoir of data to be used to advise municipalities on the effects that metallic wastes would be expected to have on their treatment procedures.

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Table 81. UNIT DIMENSIONS AND OBSERVED LOADING FACTORS
GRAND RAPIDS, MICHIGAN

Process	Design data and loading factors	
Primary clarifiers	Capacity	12 @ 16,000 ft^3 4 @ 69,500 ft^3 } 470,000 ft^3
	Detention time at 35 mgd	2.4 hr
	Surface overflow rate	745 gal/ft^2/day
	Weir overflow rate	90,200 gal/ft/day
Aeration units	Capacity	6 @ 173,000 ft^3 = 1.04×10^6 ft^3
	Detention time at 35 mgd	5.3 hr
	Loading	
	BOD	0.5 lb/day/lb VSS 16.5 lb/day/1,000 ft^3 aeration volume
	COD	1.6 lb/day/lb VSS 56.5 lb/day/1,000 ft^3 aeration volume
	MLVSS	540 mg/liter
	Air supplied	0.5 ft^3/gal sewage
Final clarifiers[a]	Capacity	6 @ 94,000 ft^3 = 565,000 ft^3
	Detention time at 35 mgd	2.4 hr
	Surface overflow rate	892 gal/ft^2/day
	Weir overflow rate	12,600 gal/ft/day
Anaerobic digestion completely mixed by gas recirculation	Capacity	1 completely mixed @ 150,000 ft^3 5 storage
	Detention time in completely mixed unit	12 days
	Loading	170 lb VS/day/1,000 ft^3
	Digested sludge	Dewatered on sand and removed to fill area or filtered and incinerated

[a] Only five clarifiers in use at time of study.

The plants were sampled for the usual measures of treatment efficiency by analyses of 24-hour composites, collected hourly by hand. An additional 8-hour composite was kept during the expected peak of flow and concentration for the 9:00 a.m. to 5:00 p.m. working day. Samples were proportioned to flow. Compositing periods for the various processes were staggered in time, on the basis of theoretical

detention times, in order to follow the flow through the plant. Sludges, because of their nonuniform nature, cyclic pumping, and hand sampling, were the most difficult to sample. All numbers reported in the text are reported to two significant figures, because the combination of sampling

Table 82. UNIT DIMENSIONS AND OBSERVED LOADING FACTORS
RICHMOND, INDIANA

Process	Design data and loading factors	
Primary clarifier	Capacity	4 @ 22,000 ft^3 ea = 88,000 ft^3
	Detention time at 7 mgd	2.3 hr
	Surface overflow rate	1,200 gpd/ft^2
	Weir overflow rate	133,000 gal/ft of weir/day
Aeration units	Capacity	7 @ 79,800 ft^3 ea = 558,000 ft^3
	Detention time at 7 mgd	14.3 hr
	Loading	
	BOD	0.09 lb/day/lb VSS 10 lb/day/1,000 ft^3 aeration volume
	COD	0.29 lb/day/lb VSS 28 lb/day/1,000 ft^3 aeration volume
	MLVSS	1,650 mg/liter
Final clarifier	Capacity	4 @ rectangular 3 @ circular } = 153,000 ft^3
	Detention time at 7 mgd	3.9 hr
	Surface overflow rate	600 gpd/ft^2
	Weir overflow rate	5,200 gal/ft of weir/day
Anaerobic digestion	Capacity	2 primary digesters - 200,000 ft^3 3 secondary digesters - 196,000 ft^3
with one primary digester in operation	Detention time in primary digester	20 days
	Loading	112 lb VS/day/1,000 ft^3

error, short sampling period in relation to a year of plant operation, and analytical error indicates that greater accuracy is not justified.

All analytical procedures employed in this study were according to *Standard Methods* (10) with the exception of those for COD, copper,

Table 83. UNIT DIMENSIONS AND OBSERVED LOADING FACTORS ROCKFORD, ILLINOIS

Process	Design data and loading factors	
Primary clarifier	Capacity	2 @ 134,000 ft^3 = 268,000 ft^3
	Detention time at 28.5 mgd	1.8 hr
	Surface overflow rate	950 gal/ft^2/day
	Weir overflow rate	143,000 gal/lineal ft of weir/day
Trickling filters (high rate)	Capacity	4 @ 150 ft dia, 5 ft deep 88,300 ft^3 ea = 353,000 ft^3
	Loading	
	BOD	85 lb/1,000 ft^3/day
	COD	252 lb/1,000 ft^3/day
	Hydraulic	28 x 10^6 gal/acre/day
Final clarifiers	Capacity	4 @ 106,000 ft^3= 423,000 ft^3
	Detention time at 28.5 mgd	1.5 hr
	Surface overflow rate	1,600 gal/ft^2/day
	Weir overflow rate	47,800 gal/lineal ft of weir/day
Anaerobic digestion (completely mixed by gas recirculation)	Capacity	4 @ 48,000 ft^3 1 @ 67,000 ft^3 } 259,000 ft^3
	Detention time	24 days
	Loading	100 lb VS/1,000 ft^3/day
	Digested sludge	Digested sludge is pumped to holding tanks and then to lagoons. Sufficient holding time is available for the formation of supernatant, which is released to the Rock River. The settled sludge is removed to fill areas when dry.

zinc, and nickel. The COD procedure used was the mercuric sulfate modification to eliminate chloride interference(32). The metals copper, zinc, and nickel were determined by utilizing a polarographic technique.

In Tables 84 through 87 the metal contents of the various process effluents of each of the four plants are given. The 24-hour composites, 8-hour composites, and the soluble metals in the 8-hour composites are tabulated for three of the plants; no 8-hour composites were collected at the Bryan plant. Comparison among the average total metal composites for the 24-and 8-hour periods shows that the receipt of metals by the municipal plants, on a concentration basis, is approximately constant throughout the day. Rockford is the only plant that shows a significantly larger metal concentration during the 9:00 a.m. to 5:00 p.m. workday over the 24-hour composite.

The relatively constant dosage of metal to the plants was an unexpected finding, but can be explained by holdup in the interceptors, varied industrial work schedules, and feedback to the process in the form of digester supernatant and waste activated sludge. For instance, at Bryan (Table 84), because of limited digester volume and full drying beds, an excessive amount of poorly settled digester supernatant was fed back to the process during the study period. This resulted in a computed metal concentration for the total plant flow several times that received via the incoming sewage. The full amount of this computed concentration of metal did not reach the aerators because most of the excess activated sludge and solids in the supernatant were recycled back to the digester with the primary sludge. Feedback is the reason there is no apparent metal removal through the primaries at Bryan and Richmond. Grand Rapids recycles a small volume of a good supernatant and a low-solids waste sludge. Rockford does not recycle digester supernatant. These latter two plants show metal removal through the primaries. The digesters and the return activated sludge act as reservoirs of the metals that continually impress a metal dosage on the biological system.

Tables 84 through 87 are based on average concentration; consequently, no accurate estimate of removal of the metals by the plant processes can be made from them, because of variable flow patterns and variable daily metal dosage.

These tables show that zinc at all four plants exists predominantly in an insoluble form. Nickel passes through the plants almost entirely in the soluble form. Chromium and copper exhibit erratic solubility behavior in the primary effluents when compared among the various plants. The metals in the final effluents are mostly in a soluble form, except for zinc in the final effluent from Rockford. This solubility pattern of the metals had been previously demonstrated in pilot plant studies (33).

Table 85. METALS IN PROCESS EFFLUENTS: GRAND RAPIDS, MICHIGAN, SEPTEMBER 1963

Source	Composite period, hr	Concentrations for 14-day period, mg/liter								
		Chromium		Copper		Zinc		Nickel		Total of 4 metals
		Avg	Range	Avg	Range	Avg	Range	Avg	Range	
Sewage										
Total metal	24	3.6	0.7–5.6	1.4	0.7–2.4	1.5	0.6–2.5	2.0	1.3–3.4	8.5
	8	3.8	0.6–5.1	1.6	0.3–3.7	1.5	0.4–2.2	2.1	1.2–3.5	9.0
Primary effluent										
Total metal	24	3.2	0.6–6.3	1.5	0.6–2.8	1.0	0.4–1.5	1.8	0.9–2.9	7.5
	8	3.5	0.6–5.3	1.4	0.4–2.3	1.0	0.4–1.6	1.9	1.0–2.4	7.8
Soluble metal	8	2.8	0.3–4.0	1.4	0.5–2.7	0.2	0.1–0.4	1.7	0.8–2.2	6.1
Final effluent										
Total metal	24	2.5	1.0–3.3	1.6	0.4–2.9	0.8	0.6–1.2	1.8	1.0–2.5	6.7
	8	2.6	1.0–3.8	1.6	0.3–3.2	0.7	0.6–0.9	1.8	1.0–2.2	6.7
Soluble metal	8	1.7	0.2–3.1	1.3	0.2–2.6	0.3	0.2–0.6	1.6	0.8–2.1	4.9
		Computed concentrations in total plant flow introduced by feedback, mg/liter								
Digester supernatant	–	0.1	–	0.01	–	0.05	–	0.01	–	0.2
Waste activated sludge	–	0.5	–	0.05	–	0.2	–	0.05	–	0.8
Sum	–	0.6	–	0.1	–	0.2	–	0.06	–	1.0

Table 84. METALS IN PROCESS EFFLUENTS; BRYAN, OHIO, DECEMBER 1963
Concentrations in 24-hr composites for 5-day period, mg/liter

Source	Metal form	Chromium		Copper		Zinc		Nickel		Total of 4 metals
		Avg	Range	Avg	Range	Avg	Range	Avg	Range	
Sewage	Total	0.8	0.6–1.1	0.2	0.2–0.3	2.2	1.4–3.0	0.05	0.03–0.1	3.3
Primary effluent	Total	0.9	0.6–1.5	0.2	0.1–0.3	1.8	1.2–2.7	0.06	0.05–0.1	3.0
	Soluble	0.5	0.1–1.2	0.1	0.05–0.2	0.3	0.1–0.5	0.06	0.03–0.1	1.0
Final effluent	Total	0.2	0.2–0.3	0.1	0.04–0.1	0.2	0.2–0.3	0.05	0.03–0.1	0.6
	Soluble	0.2	0.1–0.4	0.1	0.07–0.2	0.2	0.1–0.3	0.05	0.04–0.1	0.6
		Computed concentrations in total plant flow introduced by feedback, mg/liter								
Digester supernatant	Total	2.6	–	0.1	–	2.7	–	0.06	–	5.5
Waste activated sludge	Total	1.2	–	0.2	–	1.5	–	0.03	–	2.9
Sum	Total	3.8	–	0.3	–	4.2	–	0.1	–	8.4

Table 87. METALS IN PROCESS EFFLUENTS; ROCKFORD, ILLINOIS, OCTOBER-NOVEMBER 1963

Source	Composite period, hr	Concentrations for 13-day period, mg/liter								
		Chromium		Copper		Zinc		Nickel		Total of 4 metals
		Avg	Range	Avg	Range	Avg	Range	Avg	Range	
Sewage										
Total metal	24	1.8	0.5–2.9	1.4	0.6–3.3	2.7	1.2–3.4	0.9	0.2–1.9	6.8
	8	2.7	0.4–3.9	1.7	0.4–6.8	3.7	1.0–10	1.0	0.08–2.2	9.1
Primary effluent										
Total metal	24	1.5	0.5–2.2	1.3	0.5–2.6	2.0	0.9–3.6	0.9	0.3–1.2	5.7
	8	1.8	0.3–3.0	1.7	0.2–7.5	2.1	0.8–3.4	1.0	0.3–1.6	6.6
Soluble metal	8	1.1	0.1–2.5	1.5	0.2–5.5	0.5	0.2–1.2	0.9	0.2–1.4	4.0
Final effluent										
Total metal	24	1.2	0.6–1.5	1.0	0.5–3.6	1.3	0.8–1.7	0.9	0.5–1.4	4.4
	8	1.2	0.2–1.8	1.6	0.4–7.3	1.4	1.0–1.8	1.0	0.5–1.9	5.2
Soluble metal	8	0.6	0.05–1.5	1.2	0.2–5.5	0.2	0.1–0.5	1.0	0.6–1.5	3.0

Table 86. METALS IN PROCESS EFFLUENTS; RICHMOND, INDIANA, AUGUST 1963

Source	Composite period, hr	Chromium		Copper		Zinc		Nickel		Total of 4 metals
		Concentrations for 14-day period, mg/liter								
		Avg	Range	Avg	Range	Avg	Range	Avg	Range	
Sewage	24	0.8	0.2–2.1	0.2	0.1–0.4	0.3	0.1–0.5	0.03	0.01–0.1	1.3
Total metal	8	0.3	0.2–1.2	0.2	0.1–0.5	0.3	0.2–0.5	0.03	0.01–0.1	0.8
Primary effluent										
Total metal	24	0.8	0.3–1.8	0.3	0.2–0.6	0.4	0.3–0.9	0.03	0.01–0.05	1.5
	8	0.7	0.4–1.0	0.3	0.2–0.3	0.3	0.3–0.5	0.1	0.02–0.2	1.4
Soluble metal	8	0.3	0.01–1.2	0.1	0.2–0.3	0.1	0.04–0.1	0.04	0.01–0.1	0.6
Final effluent										
Total metal	24	0.2	0.01–0.5	0.07	0.04–0.2	0.1	0.1–0.2	0.02	0.01–0.03	0.4
	8	0.1	0.01–0.5	0.05	0.03–0.1	0.1	0.1–0.2	0.02	0.01–0.04	0.3
Soluble metal	8	0.04	0.01–0.1	0.04	0.01–0.1	0.1	0.1–0.2	0.02	0.01–0.1	0.2
		Computed concentrations in total plant flow introduced by feedback, mg/liter								
Digester supernatant	–	0.4	–	0.4	–	0.4	–	0.05	—	1.3
Waste activated sludge	–	0.4	–	0.3	–	0.3	–	0.02	–	1.3
Sum	–	0.8	–	0.7	–	0.7	–	0.07	–	2.3

The concentrations of the metals in the various sludges produced by the plants are given in Tables 88 through 91 along with the average metal content of the raw sewages. Modest amounts of the metals in the raw sewage can produce sludges containing several percent metal on a total solids basis. The mixed liquor at Richmond, the plant receiving the least amount of metal, has about the same concentration of metals as Grand Rapids, the plant receiving the most metal. This is because Richmond carries a higher mixed-liquor solids.

A unique feature of the Richmond plant is the practice of feeding the municipal garbage to the anaerobic digesters (34). The garbage amounts to 40 percent of the total volatile matter added, but the metal content is so low that only 1 percent of the metals added to the digester comes from the garbage (Table 90).

Table 88-A. METAL CONTENT OF SLUDGES PRODUCED BY BRYAN PLANT

Type	Chromium		Copper		Zinc		Nickel	
	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g
Primary sludge	125	5	36	1	242	12	2	0.05
Excess activated sludge	17	5	2	0.7	20	6	0.1	0.04
Mixed liquor	9	–	1	–	10	–	0.07	–
Digesting sludge	88	4	27	1	220	11	2	0.1
Digester supernatant	77	4	4	0.6	82	7	2	0.1
	Soluble metals							
Digesting sludge	0.1	–	0.1	–	0.2	–	0.05	–

Table 88-B. METALS IN RAW SEWAGE

Metal	Chromium	Copper	Zinc	Nickel
Average concentration of metal entering plant, mg/liter	0.8	0.2	2.2	0.05

Table 89-A. METAL CONTENT OF SLUDGES PRODUCED BY GRAND RAPIDS PLANT

Type	Chromium		Copper		Zinc		Nickel	
	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g
Primary sludge	510	9	107	2	317	5	125	2
Excess activated sludge	152	17	16	2	48	5	14	2
Mixed liquor	20	–	4	–	7	–	4	–
Digesting sludge	386	11	88	3	232	7	97	3
Digester supernatant	50	10	12	2	38	8	8	2
	Soluble metals							
Digesting sludge	0.2	–	0.3	–	0.2	–	0.8	–

Table 89-B. METALS IN RAW SEWAGE

Metal	Chromium	Copper	Zinc	Nickel
Average concentration of metal entering plant, mg/liter	3.6	1.4	1.5	2.0

Table 90-A. METAL CONTENT OF SLUDGES PRODUCED BY RICHMOND PLANT

Type	Chromium		Copper		Zinc		Nickel	
	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g
Primary sludges	103	3	116	3	94	3	8	0.2
Excess activated sludge	34	3	22	2.6	23	3	1.5	0.1
Mixed liquor	12	–	8	–	9	–	0.4	–
Digesting sludge	95	3	88	3	73	3	4	0.2
Digester supernatant	39	–	40	–	40	–	5	–
Garbage	–	0.005	–	0.02	–	0.2	–	0.008
	Soluble metals							
Digesting sludge	0.03	–	0.4	–	0.1	–	0.1	–

Table 90-B. METALS IN RAW SEWAGE

Metal	Chromium	Copper	Zinc	Nickel
Average concentration of metal entering plant, mg/liter	0.8	0.2	0.3	0.03

Table 91-A. METAL CONTENT OF SLUDGES PRODUCED BY ROCKFORD PLANT

Type	Chromium		Copper		Zinc		Nickel	
	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g	mg/liter	mg/g
Primary sludge	271	5	108	2	395	11	27	0.5
Secondary sludge	9	7	6	4	12	8	1	0.8
Trickling filter slime	–	18	–	13	–	17	–	3
Digesting sludge	358	8	105	2	390	10	28	0.5
Digester supernatant	14	–	3	–	24	–	2	–
	Soluble metals							
Digesting sludge	0.8	–	1.0	–	0.7	–	–	Nil

Table 91-B. METALS IN RAW SEWAGE

Metal	Chromium	Copper	Zinc	Nickel
Average concentration of metal entering plant, mg/liter	1.8	1.4	2.7	0.9

METAL BALANCES

At each of the plants metal balances were performed. The balances shown in Tables 92 through 95 are for 2-week periods, except that of Bryan, which is from a special study of a prearranged slug of chromium to this plant (35). One-hundred and fifty gallons of a spent plating bath containing 50 pounds of hexavalent chromium as CrO_3 was dumped to the municipal sewer and traced through the Bryan plant.

The balance figures for each of the plants are given in pounds to indicate the actual quantities of metals that are handled by municipal plants.

Table 92. BRYAN, OHIO
METAL BALANCE FOR DAY OF CHROMIUM SLUG
50 POUNDS AS CrO_3 DUMPED TO SEWER

Source	Chromium, lb
Sewage	47
Primary effluent	37
Primary sludge (by difference)	10
Aeration tanks	25
Waste sludge	4
Final effluent	10
% of chromium accounted for	94
% of chromium retained by plant (1-day basis)	80

Table 93. GRAND RAPIDS, MICHIGAN, METAL BALANCE FOR 14 DAYS

Source of metals	Quantity of metal in 14 days, lb			
	Chromium	Copper	Zinc	Nickel
Sewage	15,500	6,240	6,540	8,440
Digester supernatant	250	60	190	40
Waste activated sludge	2,040	216	650	194
Aeration tanks	–20	+100	–40	–5
Total quantity added	17,770	6,516	7,340	8,669

Final effluent	10,600	6,440	3,110	7,580
Primary sludge	4,970	1,040	3,090	1,220
Total in outlets	15,570	7,480	6,200	8,800

Outlet for metal	Percent of metal added			
	Chromium	Copper	Zinc	Nickel
Final effluent	60	99	43	87
Primary sludge	28	16	42	14
% accounted for	88	115	85	101
% removal by plant, from total quantity added	40	≃16	58	12

Table 94. RICHMOND, INDIANA,
METAL BALANCE FOR 14 DAYS ON PRIMARY (A)
OVERALL REMOVAL BY PLANT FOR SAME PERIOD (B)

	Source of metals	Quantity of metals in 14 days, lb			
		Chromium	Copper	Zinc	Nickel
PART A	Sewage	559	180	262	20
	Digester supernatant	287	288	274	33
	Waste activated sludge	326	218	229	15
	Total quantity added	1,172	686	765	68
		Balance on primary			
	Primary effluent	630	255	326	24
	Primary sludge	406	460	372	33
	Total quantity found	1,036	715	698	57
	% accounted for	88	104	91	84
PART B		Overall removal by plant			
	lb in final effluent	210	50	112	15
	% removal by plant, from total quantity added	82	73	85	78

Table 95. ROCKFORD, ILLINOIS,
METAL BALANCE FOR 13 DAYS

Source of metals	Quantity of metals in 13 days, lb			
	Chromium	Copper	Zinc	Nickel
(In)				
Sewage	5,837	4,502	8,458	2,860
(Out)				
Final effluent	3,662	3,483	3,968	2,630
Primary sludge	2,294	927	3,360	230
Total	5,956	4,410	7,328	2,860
Outlet for metal	**Percent of metal added**			
	Chromium	Copper	Zinc	Nickel
Final effluent	63	77	47	92
Primary sludge	39	21	40	8
% accounted for	102	98	87	100
% removal by plant	37	23	53	8

The balance for Grand Rapids (Table 93) is very striking when it is realized that in the 2-week study period approximately 18 tons of the metals entered the plant.

The balance for Richmond (Table 94) shows very clearly the amount of metal feedback to the system by the digester supernatant and waste sludge. A balance on the complete plant could not be made because of the loss of one of the aerator samples; however, the balance through the primary gives a satisfactory account of the metals.

The percent removals of the individual metals at Rockford (Table 95), and Grand Rapids are similar. Richmond shows higher removals than the other plants; however, the quantity received by this plant is much less than that by the others. At each of the plants zinc is most effectively removed and nickel least. This was expected from pilot plant studies (33). Copper and chromium are less effectively removed than expected. In general, all the removals are less than indicated by the pilot studies, with the exception of the Richmond removals.

AEROBIC EFFICIENCY OF PLANTS

Tables 96 through 99 give the average characteristics of the various raw sewages and plant effluents; also tabulated are the percent removals from raw sewage to primary and final effluents. Richmond and Bryan show excellent overall efficiency. The removals in the primaries at these plants are not so good as the primary removals at Grand Rapids and Rockford. This is another reflection of the higher-than-usual feedback of digester supernatant to the primaries at Richmond and Bryan.

The lower overall removal efficiency at the Grand Rapids plant is believed to be due to its inability to maintain a suitable mixed liquor solids because of a limited return-sludge pumping capacity. This results in a young, nonflocculant sludge and a turbid effluent

Table 96. BRYAN, OHIO
AVERAGE CHARACTERISTICS OF SEWAGE AND EFFLUENTS
FOR 5 DAYS

Analysis	Raw sewage		Primary clarifier effluent			Final clarifier effluent		
	Avg, mg/liter	Range, mg/liter	Avg, mg/liter	Range, mg/liter	Removed, %	Avg, mg/liter	Range, mg/liter	Removed, %
BOD	325	275–359	216	182–256	33	25	20–30	92
COD	603	481–754	451	391–517	25	90	85–96	85
Suspended solids	164	100–216	141	98–166	14	25	21–30	85
Turbidity	–	–	–	–	–	49[a]	32–60[a]	–

[a] In stu.

with high suspended solids (Table 97). Moreover, the Grand Rapids plant is the only one of the three activated-sludge plants studied that has a hydraulic load approaching design capacity.

Table 97. GRAND RAPIDS, MICHIGAN,
AVERAGE CHARACTERISTICS OF SEWAGE AND EFFLUENTS
FOR 14 DAYS

Parameter	Raw sewage		Primary clarifier effluent			Final clarifier effluent		
	Avg, mg/liter	Range, mg/liter	Avg, mg/liter	Range, mg/liter	Removed, %	Avg, mg/liter	Range, mg/liter	Removed, %
BOD	96	65–147	61	45–80	36	24	19–26	75
COD	314	276–415	202	152–303	36	103	70–125	67
Suspended solids	163	124–244	91	46–156	44	62	26–94	62
Turbidity	–	–	–	–	–	92[a]	71–124[a]	–

[a] In stu.

Table 98. RICHMOND, INDIANA,
AVERAGE CHARACTERISTICS OF SEWAGE AND EFFLUENTS
FOR 14 DAYS

Parameter	Raw sewage		Primary effluent			Final effluent		
	Avg, mg/liter	Range, mg/liter	Avg, mg/liter	Range, mg/liter	Removed, %	Avg, mg/liter	Range, mg/liter	Removed, %
BOD	113	68–179	95	66–153	16	9	3–16	92
COD	258	178–380	266	163–374	0	33	19–47	87
Suspended solids	194	124–282	166	84–334	14	19	6–28	90
Turbidity	–	–	–	–	–	12[a]	8–16[a]	–

[a] In stu.

Table 99. ROCKFORD, ILLINOIS
AVERAGE CHARACTERISTICS OF SEWAGE AND EFFLUENTS
FOR 13 DAYS

Parameter	Raw sewage		Primary clarifier effluent			Final clarifier effluent		
	Avg, mg/liter	Range, mg/liter	Avg, mg/liter	Range, mg/liter	Removed, %	Avg, mg/liter	Range, mg/liter	Removed, %
BOD	128	105–166	98	78–126	23	48	38–67	63
COD	370	330–490	293	226–512	21	153	121–231	59
Suspended solids	189	118–286	105	60–120	44	71	36–104	62
Turbidity	–	–	–	–	–	75[a]	53–139[a]	–

[a] In stu.

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The high-rate trickling filter plant at Rockford shows the lowest overall organic treatment efficiency, as would be expected.

The removal efficiencies of all the plants were calculated on the basis of raw sewage, and the extra loads imposed by digester supernatant and waste activated sludge were not considered.

These efficiencies are based only on a limited sampling period, and the efficiencies of the plants on a yearly basis may be significantly different than reported here. Previous pilot studies have shown that the concentrations of metals encountered in these studies would cause only about a 5 percent reduction in overall efficiency (33).

ANAEROBIC EFFICIENCY OF PLANTS

During this series of field surveys, three of the plants were encountering varying degrees of operating difficulties with their anaerobic treatment. As previously mentioned, Bryan had full drying beds and limited digester volume. One of the two primary digesters at Richmond was out of operation because of fouling by plastic wrappers introduced with the garbage feed (36). Owing to this reduced capacity, sufficient time for formation of good digester supernatant in the secondary digesters was not available. One of the digesters at Rockford was undergoing modification for conversion to gas mixed operation, and a second had just begun operation; consequently, part of the gas produced was vented unmetered. The other three mixed digesters at Rockford were producing sludge with satisfactory drainability, but the high volatile acid content indicates a condition requiring close control. The digesters at Rockford have been followed for 4 years by this laboratory, and a volatile acid content of 2,000 milligrams per liter is characteristic of their behavior.

The digesters at Grand Rapids, which contained the most metals of all the plants studied (Table 89), were functioning in an excellent manner, producing a workable sludge with a low volatile content, good gas production, and a satisfactory relation among volatile acids, alkalinity, and pH. The Grand Rapids digesters have been followed for 3 years by this laboratory, and the plant chemist has reported on the composition and use of the gas produced (37).

On the bases of experience with the Grand Rapids digesters and pilot investigations (33), the concentrations of metals encountered in these field studies cannot alone be responsible for any difficulties with anaerobic digestion of the sludges.

Tables 88 through 91, which give the metal content of the various sludges at these plants, indicate that even though the digesting sludges contain several percent metal, not one of them has a soluble metal content above 1 milligram per liter. Table 100 shows the characteristics of the digesting sludges at the various plants.

Table 100. CHARACTERISTICS OF DIGESTING SLUDGES

Digester location	pH	Alkalinity (CaCO$_3$), mg/liter	Volatile acids (Acetic), mg/liter	% volatile matter	Gas, ft^3/lb VS added/day
Rockford, Illinois	6.2	6,500	3,500	59	Part unmetered
Grand Rapids, Michigan	7.4	2,500	445	51	9.5
Richmond, Indiana	7.0	630	400	58	8.3
Bryan, Ohio	6.8	1,800	800	50	Part unmetered

SLUGS OF METALS

At each of the plants, slugs of metals or metal cyanide complexes were encountered. At Richmond, during the 2-week study, several yellowish-green slugs were noted and sampled. The grab samples were then correlated with the amount of chromium received daily by the plant. Figure 81 shows the pounds of chromium entering the plant each day. The greater daily quantities correspond to the detected slugs of chromium. The concentration of chromium in the grab sample and the time of the slug are also shown. The slugs always occurred in the evening and after normal working hours. During the first week, the largest daily quantities entered the plant on the weekend. Analyses of these grab samples showed that chromium was the major metallic constituent. Analyses of the 24-hour composite samples for cyanide indicated that, during this study period, only a small amount of cyanide was received by the plant.

The receipt of a planned slug of chromic acid to the Bryan plant is recorded in Figure 73, graphed from the data compiled on the day of the slug. Analyses of the daily composites for the entire 5 days of the study, given in Figure 80, showed that in addition to this planned slug of chromium, a nonplanned copper cyanide complex slug occurred 2 days later. The complex imparted no color to the sewage and went unnoticed until later laboratory analysis. In Figure 80 the difference between the 24-hour composite concentrations of chromium in the primary effluent and the raw sewage was due to the method of sampling. The 24-hour composite samples were made up of 24

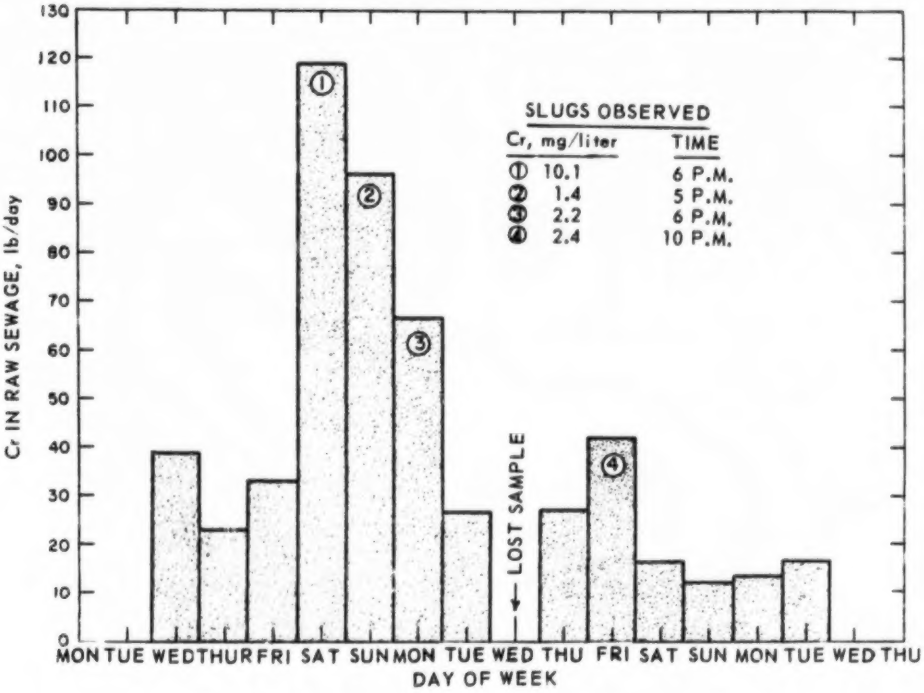

Figure 81. Daily variation of chromium, Richmond, Ind.

hourly grabs taken on the hour. A sample of raw sewage was taken while the slug was in progress. Since 95 percent of the chromium entered the plant in 25 minutes (Figure 73) and the entire slug lasted only 1 hour, this was the only grab sample of the sewage containing chromium from the slug. In the case of the primary effluent, in which the slug lasted for 12 hours, 12 samples that had chromium from the slug were taken for compositing. This would account for the higher 24-hour-composite concentration in the primary effluent.

The same reasoning applies to the copper slug, except that the sewage sample must have been taken at the peak concentration of the complex in the sewage, which introduced more copper into the sewage composite in one grab than several grabs of primary effluent did for its 24-hour composite.

If both slugs had occurred shortly after the hour and ended shortly before, the 24-hour raw sewage composites would not have indicated their presence.

The recorded slugs did not produce any significant effect on the treatment efficiency of the Bryan plant. This agrees well with the past experience of the plant superintendent and pilot investigations (8, 13, 38).

Several slugs were caught at the Grand Rapids plant. Since the color of the sewage was the signal to collect a grab for analysis, again at Grand Rapids, chromium was the most common slug detected. Table 101 shows the record of these slugs. One analysis shows, however, that in addition to the chromium there was a respectable concentration of zinc in the September 25 sample. Samples of composites analyzed for cyanide showed an average concentration of 1 milligram per liter during this 2-week period.

Table 101. SLUGS OF METALS IN INFLUENT SEWAGE, GRAND RAPIDS, MICHIGAN

Date (1963)	Time	Metal, mg/liter			
		Chromium	Copper	Zinc	Nickel
9–20	10 p.m.	12.6	1.2	2.0	2.6
9–25	3 a.m.	3.2	1.2	9.3	2.1
9–28	10 a.m.	25.8	0.5	1.0	0.7
9–28	11 p.m.	3.1	1.0	1.6	1.2
10–1	7 a.m.	14.6	0.6	1.0	1.7

Rockford has a history of receiving cyanide and metal cyanide complexes (39). While this study was in progress, a slug of metal cyanide complexes hit the plant and is recorded in Table 102, Part A. The officials of the plant had informed the study team that the plant had been receiving cyanide slugs for several months previous to the study. The 11:00 a.m. grab sample was taken for routine analysis. When a fish kill in the Rock River was reported in the early evening of October 23, downstream from the plant outfall, the additional grabs and composites listed in the table were analyzed for cyanide by the plant chemist. Part B of this table shows the concentrations of cyanide detected in the Rock River at the time of the fish kill. Judged by the concentrations of metals and cyanide in the 11:00 a.m. grab and the 8-hour composite, a slug containing a mixture of copper and zinc, probably as the cyanide complexes, entered the plant in the late morning period. During this portion of the year, the Rock River drainage area was in the midst of a dry spell, and the usual dilution afforded by the river was not available. The slug caused no significant decrease in the efficiency of the trickling filter performance for that day, as compared with the average efficiency of the filter for the 2-week period.

The slug data for Richmond and Grand Rapids point out that even though the presence of a slug of chromium can be detected by the yellowish-green color of the sewage, the actual concentration of the metal may not be very large. Apparently 1.5 to 3 milligrams of chromium per liter can be noted by eye.

Table 102. ROCKFORD, ILLINOIS
SLUG OF METAL COMPLEXES

Part A-Plant samples

Date (1963)	Time	Location	Metals and cyanide, mg/liter				
			Chromium	Copper	Zinc	Nickel	Cyanide
10-22 to 10-23	24-hr composite	Sewage	2.2	1.7	3.4	0.9	–
10-23	11 a.m. grab	Sewage	2.9	0.7	7.9	2.2	9.8
10-23	8-hr composite 12-8 p.m.	Primary effluent	2.2	7.5	3.4	1.3	16.3
0-23	8 p.m. grab	Sewage	5.8	1.5	3.1	1.1	3.0
10-23 to 10-24	24-hr composite	Final effluent	1.4	1.1	1.6	1.4	3.8

Part B-Rock River samples

Date (1963)	Time	Location	Metals and cyanide, mg/liter				
			Chromium	Copper	Zinc	Nickel	Cyanide
10-23	8 p.m.	1.9 miles upstream	0.09	0.05	0.07	Nil	Nil
10-23	7:15 p.m.	0.3 mile downstream	0.14	0.46	0.14	0.01	0.3
10-23	7:45 p.m.	2.2 miles downstream	0.24	1.19	0.24	0.10	1.4
10-24	2:30 p.m.	0.3 mile downstream	0.16	0.17	0.25	0.04	Nil
10-24	3 p.m.	2.2 miles downstream	0.59	0.05	0.01	0.02	Nil

The slug data for all four plants show that the biological systems are tolerant to moderate slug conditions; however, the Rockford study points out the necessity of considering the effects that discharge of the final effluent will have on the receiving water.

NITRIFICATION

Only one of the four plants, Richmond, produced a nitrified effluent. The other plants discharged their effluent nitrogen largely as ammonia. Complete analyses for the various nitrogen forms, or nitrogen balances, were not carried out. Table 103 clearly indicates that nitrification was active only at Richmond. Heavy metals at a concentration of approximately 5 milligrams per liter have previously been shown to produce a pronounced inhibition of nitrification (30).

Table 103. NITROGEN FORMS IN FINAL EFFLUENTS[a]

Location	Total Kjeldahl nitrogen	Ammonia nitrogen	Nitrate nitrogen	Dissolved oxygen final settler
Bryan, Ohio	Nil	20	Nil	0.5
Grand Rapids, Michigan	18	10	Nil	0.5
Richmond, Indiana	4	2	8	1.9
Rockford, Illinois	19	11	Nil	2.6

[a] In mg/liter.

The lack of nitrification at the other three plants cannot be conclusively correlated with inhibition of the metals, because of the many variables between these plants. Of the four plants, judged solely by observation of operating conditions, Richmond would be the one expected to nitrify. This is because of the high aerator solids, adequate detention time, small amount of heavy metals, satisfactory DO aided in part by cascade flow of mixed liquor through drop pipes down three tiers of aerators (34) and the warm season of the year at the time of the study at Richmond.

SUMMARY

A survey of four municipal treatment plants, concerning the receipt of heavy metals, distribution of the metals in the various process outlets, and effects of the metals on the treatment efficiency, has shown satisfactory correlation with pilot-plant investigations.

The results show that the plants receive metallic constituents on an almost continuous concentration basis. Several slug discharges of metals to each of the plants were also recorded. At two of the plants, digester supernatant accounted for a considerable portion of the metal in the process. The findings indicate that in the range of 1 to 9 milligrams per liter heavy metals cause no serious reduction in efficiency of the aerobic or anaerobic treatment of sewage.

In these studies at operating municipal plants many uncontrollable variables were encountered, but the pattern of response of the plants was similar to the 100-gallon-a-day pilot studies.

REFERENCES

1. Standard Methods for the Examination of Water, Sewage, and Industrial Wastes. 10th ed. Am. Public Health Assn. New York. 1955.

2. Udy, M. J. Chemistry of Chromium and Its Compounds. In: Chromium, Vol. 1. Reinhold Publishing Corp. New York. 1956. p. 120.

3. Jenkins, S.H., and Hewitt, C.H. The Effect of Chromium Compounds on the Purification of Sewage by the Activated-Sludge Processes. J. Inst. Sewage Purif. (Midland Branch). 222. 1942.

4. Edwards, G. P., and Nussberger, F. E. The Effect of Chromate Wastes on the Activated-Sludge Process at the Tallmans Island Plant. Sewage Works J. 19 (4):598. July 1947.

5. Placak, O. R., Ruchhoft, C. C., and Snapp, R. G. Copper and Chromate Ions in Sewage Dilutions. Ind. Eng. Chem. 41:2238. 1949.

6. Coburn, S. E. Limits for Toxic Wastes in Sewage Treatment. Sewage Works J. 21(3):522. May 1949.

7. Genter, A. L. Adsorption and Flocculation as Applied to Sewage Sludges. Sewage Works J. 6(4):689. July 1934.

8. Moore, W. A., McDermott, G. N., Post, M. A. et al. Effects of Chromium on the Activated-Sludge Process. JWPCF. 33:54. Jan. 1961.

9. Gray, A. G. Modern Electroplating. John Wiley & Sons, Inc. New York. 1953.

10. Standard Methods for the Examination of Water and Wastewater. 11th ed. Am. Public Health Assn. New York. 1960.

11. Gameson, A. L. H., Truesdale, G. A., and Van Overdijk, M. J. Variation in Performance of Twelve Replicate Small-Scale Percolating Filters. J. Inst. Sewage Purif. Part 4. 342. 1961.

12. Ludzack, F. J., Schaffer, R. B., and Bloomhuff, R. N., Experimental Treatment of Organic Cyanides by Conventional Processes. JWPCF. 33:492. May 1961.

13. McDermott, G. N., Moore, W. A., Post, M. A., and Ettinger, M. B. Effects of Copper on Aerobic Biological Sewage Treatment. JWPCF. 35:227. Feb. 1963.

14. Ridenour, G. M., Backus, R. D., and Sherron, C. Effect of Polysulfide Treated Cyanide Case Hardening, Copper and Zinc Plating Wastes on Sludge Digestion. Sewage Works J. 17 (5):966. Sept 1945.

15. Taylor, C. G. Determination of Small Quantities of Nickel with α - Furildioxime. Analyst. 81:369. June 1956.

16. McDermott, G. N., Barth, E. F., Salotto, B. V., and Ettinger, M. B. Zinc in Relation to Activated-Sludge and Anaerobic Digestion Processes. Proc. 17th Ind., Waste Conf., Lafayette, Ind. May 1-3, 1962. Eng. Ext. Ser. 112. Eng. Bull., Purdue Univ. 47 (2):461 Mar. 1963.

17. McDermott, G. N., Post, M. A. Jackson, B. N. and Ettinger, M. B. Nickel in Relation to Activated-Sludge and Anaerobic Digestion Processes. JWPCF. 37:163. Feb. 1965.

18. McDermott, G. N., Moore W. A., Post, M. A., and Ettinger, M. B. Copper and Anaerobic Sludge Digestion. JWPCF. 35:655. May 1963.

19. Mancy, K. H., Westgarth, W. C., and Okun, D. A. The Applications of the Galvanic Cell Oxygen Analyzer to Waste Control Programs. Proc. 17th Ind. Waste Conf., Lafayette, Ind. May 1-3, 1962. Eng. Ext. Ser. 112. Eng. Bull., Purdue Univ. 47 (2):508. Mar. 1963.

20. Bozich, T. A. The Toxicity of Metals on the Activated-Sludge Process. Master's Thesis. Case Inst. Technology. Cleveland, Ohio. 1959.

21. Masselli, J. W., Masselli, N. W., and Burford, G. The Occurrence of Copper in Water, Sewage, and Sludge and Its Effects on Sludge Digestion. New England Interstate Water Pollution Control Commission, 73 Tremont Street, Boston, Mass, June 1961.

22. Dawson, P. S., and Jenkins, S. H. The Oxygen Requirements of Activated-Sludge Determined by Manometric Methods. Sewage and Ind. Wastes. 22:490. 1950.

23. Jenkins. S. H. Trade Waste Treatment. J. Inst. Sewage Purif. Part 2. 193. 1957.

24. Tarvin, D. Metal Plating Wastes and Sewage Treatment. Sewage and Ind. Wastes. 28:1371. 1956.

25. Stones, T. The Fate of Chromium During the Treatment of Sewage. J. Inst. Sewage Purif, Part 4. 435. 1955.

26. Stones, T. The Fate of Copper During the Treatment of Sewage. J. Inst. Sewage Purif. Part 1. 82. 1958.

27. Stones, T. The Fate of Nickel During the Treatment of Sewage. J. Inst. Sewage Purif. Part 2. 252. 1959.

28. Stones, T. The Fate of Zinc During the Treatment of Sewage. J. Inst. Sewage Purif. Part 2. 254. 1959.

29. Pettet, A. Effect of Metal Finishing Wastes on Sewage Purification. J. Inst. Sewage Purif. Part 1. 36. 1956.

30. Barth, E. F., Salotto, B. V., McDermott, G. N., et al. Effects of a Mixture of Heavy Metals on Sewage Treatment Processes. Proc. 18th Ind. Waste Conf. Lafayette, Ind. April 30-May 2, 1963. Eng. Ext. Ser. 115. Eng. Bull., Purdue Univ. 48(3):616. May 1964.

31. Ettinger, M. B. Heavy Metals in Waste-Receiving Systems. Presented at Interdepartmental Natural Resources Seminar, Ohio State Univ. Columbus, Ohio, March 1963.

32. Dobbs, R. A., and Williams, R. T. Elimination of Chloride Interference in the Chemical Oxygen Demand Test. Anal. Chem. 35:1064. July 1963.

33. Barth, E. F., Ettinger, M. B., Salotto, B. V., and McDermott, G. N. Summary Report on the Effects of Heavy Metals on the Biological Treatment Processes. JWPCF. 37:86. Jan. 1965.

34. Ross, W. E., and Steeg, H. R. Richmond, Ind., Solves Its Garbage-Sewage Problems. Am. City. 67:132. Sept. 1952.

35. English, J. N., Barth, E. F., Salotto, B. V., and Ettinger, M. B. A Slug of Chromic Acid Passes Through A Municipal Treatment Plant. Presented at 19th Ann. Purdue Ind. Waste Conf. Lafayette, Ind. May 5-7, 1964.

36. Wahl, A. J. Larson, C. C., Neighbor, J.B., et al. 1963 Operators' Forum, JWPCF. 36:401. Apr. 1964.

37. The Round Table. Discussion by Doris Voshel., Grand Rapids, Mich. Wastes Eng. 34:362. July 1963.

38. Phillips, M. B. Activated-Sludge Response to Excess Chromium Waste. Presented at 38th Ann. Ohio Water Pollution Control Conf. Cincinnati, Ohio. 1964.

39. Carlson, P. R. Cyanide Waste Disposal Survey. Sewage and Ind. Wastes. 24:1541. Dec. 1952.

40. Salotto B. V., Barth, E.F., Tolliver, W.E., and Ettinger, M.B. Organic Load and Toxicity of Copper to Activated-Sludge Process. Presented at 19th Ann. Purdue Ind. Waste Conf. Lafayette, Ind. May 5-7, 1964.

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